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INTERIM TECHNICAL DOCUMENTARY PROGRESS REPORT **2**

29 SEPTEMBER 1962 through 28 DECEMBER 1962

CONTRACT AF33(657)-8789

PROJECT 7-935

DIFFUSION BONDING

OF REFRACTORY METALS

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Submitted to **Fabrication Branch**
Manufacturing Technology Laboratory
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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2 JANUARY 1963

RDR 1322-2

SOLAR

A SUBSIDIARY OF INTERNATIONAL HARVESTER COMPANY

ABSTRACT SUMMARY

DIFFUSION BONDING OF REFRACTORY METALS

A. G. Metcalfe and T. B. Lindemer,
Solar
A subsidiary of International Harvester Company

Six concepts to actuate the diffusion bonding process have been evaluated experimentally. Three of these surface active elements, recrystallization of cold worked metal, and allotropic transformations promote bonding. Small atom diffusion aids, acceleration of diffusion by a high frequency field, and bonding under subsolidus conditions are ineffective or inapplicable to refractory metal bonding. The magnitude of improvement of joints with intermediate foils that recrystallize or undergo allotropic transformation has been found to be small, whereas surface active elements produce a severalfold increase in bond strength.

A survey of refractory metal structures and the design of joints to build these structures has been started. It has been concluded from this work that new joint designs will be needed to take full advantage of the diffusion bonding process. Special tooling to make joints is under construction. This special tooling will be used to study the bonding of refractory metals and to provide data for the construction of more advanced bonding equipment.

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FOREWORD

This Interim Technical Documentary Report covers work performed under Contract AF33(657)-8789 from 29 September 1962 through 28 December 1962. It is published for technical information only and does not necessarily represent the recommendations, conclusions, or approval of the Air Force.

This contract with the Research Laboratories of Solar, a subsidiary of International Harvester Company, San Diego, California, was initiated under Aeronautical Systems Division (ASD), Manufacturing Technology Laboratory Project 7-935, "Joining of Refractory Metals." It is administered under the direction of Mr. G. E. Eichelman, Manufacturing Technology Laboratory, Fabrication Branch (ASRCTF).

Dr. A. G. Metcalfe, Associate Director of Solar Research, is Principal Investigator for the program. Major contributions were made by T. B. Lindemer (bonding), M. R. Licciardello (structures and joints), F. K. Rose (tooling), and L. Nedosik and C. Antonick (experimental work).

Approved:

John V. Long, Director
Research Laboratories

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I. INTRODUCTION

The development of high performance, high speed, aerospace vehicles for the United States Air Force will require structures to withstand intense aerodynamic heating. The refractory metals are the logical candidates for these structures and several study programs have examined the fabrication problems and performance of refractory metal structures. Because of the inadequate oxidation resistance of the refractory metals at high temperatures, coatings are necessary. These coatings can have the required degree of reliability only if all stages of the fabrication are considered as a whole. Many, otherwise, excellent joining methods have not been considered in these structures because of their adverse effect on coating reliability. The unknown effects of braze alloys on coatings, and the difficulty of coating the re-entrant surfaces generated by spot- or seam-welding come to mind immediately. Other joining methods introduce damage to the refractory alloy, such as recrystallization and other embrittlement effects on welding. The latter problem is so acute that a weldability test is included before any columbium alloy is included in the Materials Advisory Board (MAB) panel program on refractory sheet metal alloys.

Mindful of such problems, the Fabrication Branch of the Manufacturing Technology Laboratory has placed this contract at Solar to examine the merits of diffusion bonding and to determine its place in the joining of refractory metals. In the diffusion bonding method, joints are made by pressing surfaces together at high temperature so that a bond grows across the interface by diffusion. The advantages foreseen for this method of joining are: the absence of recrystallization; the control of bonded area to avoid re-entrant surfaces (as in spot welding or riveting) because bonding can be achieved across the entire lap area; and avoidance of harmful coating-filler metal interaction such as may occur between braze alloys and coatings. The objectives of this program, then, are to make bonds between refractory metals without recrystallization of the refractory metal, to bond over the entire lap area, and to develop a rapid, economical process for the production of these bonds.

These objectives will be met by a three-phase program to develop preprocessing techniques, diffusion bonding techniques, and tooling and test fixtures. From these developments, manufacturing processes for joining the refractory metals by solid state diffusion bonding will be established. The three phases are:

Phase I - Survey and analysis

Phase II - Principal fabrication effort

Phase III - Equipment, testing, and quality control

Phase I has been accomplished by a literature survey followed by experimental examination of the concepts derived from the literature survey. The first Interim Report (Ref. 1) presented the findings of the literature survey and analysis. One of the main reasons for interest in diffusion bonding is the avoidance of recrystallization and embrittlement of refractory metals that occur in joining processes such as welding and high temperature brazing. However, bonding below the recrystallization temperature presents a dilemma. The general relationship between strength and homologous temperature indicates that no low melting point phases can be tolerated in the final joint. On the other hand, there is a general relationship between diffusion rate and melting point that suggests joints cannot be made rapidly at low temperatures with highly refractory alloys. A major purpose of the literature survey and analysis was to uncover methods to "activate" the process to circumvent this problem. Six methods were uncovered and the evaluation of these has been a major task in the last quarterly period. This work is reported under Phase I activities in the body of this report.

Approval to proceed with Phase II was received in November and work has started on several tasks. A review of refractory metal structures has been made. This review has indicated certain directions that should be followed in the development of joining processes, but it has become apparent that joint designs, currently in use, are frequently dictated by available joining methods. More efficient joints, than those currently in use, can be added to the program. Another important task started in this quarter has been the development of tooling. The bonder used in all work to date has been heated by induction and gives precise control of temperatures, times, and pressures so that it is primarily a research tool. A resistance-heated

bonder has been built that will permit certain prototype joints to be made. One of the main purposes of this tool will be to establish parameters for the construction of more advanced tooling such as a seam bonder. The development of the resistance bonder will permit the rate of joint development to be increased considerably.

Other problems considered in this quarter are the coating and testing of joints. Preliminary work suggests that these two problems may be among the most severe to be solved in the program.

II. WORK ON PHASE I - SURVEY AND ANALYSIS

2.1 LITERATURE SURVEY

It has been established that diffusion bonding is a two-stage process: the first stage is largely mechanical in nature and involves plastic deformation at the interfaces to achieve intimacy of contact and disrupt surface films; the second is the strengthening of this contact by diffusion. Rapid bonding (Ref. 1) can be achieved by surpassing the Hertzian yield stress of either the refractory metal or of an intermediate foil to establish the necessary intimacy of contact, and by rapid diffusion across the interface where intimacy of contact has been established. A major purpose of the literature survey has been to find ways to obtain the necessary diffusion rapidly. The physical concepts that might permit an increase in the rate of diffusion were identified as:

• Surface activity (surface and grain boundary diffusion)	Concept 1
• Diffusion aids (small atoms with high diffusion rate)	Concept 2
• Cold work effects	Concept 3
• High frequency effects	Concept 4
• Allotropic transformation effects	Concept 5
• Subsolidus effects	Concept 6

Concept 6 was introduced to reduce the load requirement to achieve intimacy of contact, but may increase the rate of diffusion if transient melts are formed.

Further discussion and evaluation of these concepts is presented in Section 2.3.

2.1.1 Continuation of Survey

Several additional reports have been obtained and reviewed in the last quarter. These include many of the internal Battelle Memorial Institute (BMI) Reports. Detailed examination did not reveal any new information other than that already available in the various BMI and DMIC reviews of diffusion bonding.

A paper of unusual interest has appeared recently. Written by E. E. Underwood (Ref. 2), it includes 56 references, largely from Russian sources, to work on the occurrence of unusual plasticity at certain types of metallurgical transformation. The abnormal ductility of iron and its alloys at the alpha/gamma transformation, the high ductility of metals and alloys deformed during recrystallization, anomalous creep ductility near the solubility limit, and the enhanced ductility at eutectoid transformations are the principal types of superplasticity reviewed. Metastability appears to be the common line between these phenomena. Certain measurements indicate a relationship between the ductility and the degree of metastability. Thus, deJong and Rathenau (Ref. 3) found that the tensile elongation in an iron-carbon alloy, deformed while undergoing periodic partial transformation in the alpha and gamma phase region, was proportional to the amount of material transformed. Other investigators (Ref. 4) find that the ductility depends on the change of lattice parameter between the metastable and stable states. It is also found that materials are mechanically weak when transforming to a stable state.

The review paper by Underwood does not suggest any radically new concepts that should be investigated, but indicates new ways to take advantage of Concepts 3 and 5, and provides increased understanding of the effects of these concepts. Also, it casts some doubt on the exact interpretation of the effects observed and reported in the next section.

2.2 ANALYSIS OF CONCEPTS

The six concepts derived from the literature study to activate the diffusion bonding process have been examined experimentally for inclusion in Phase II. The evaluation of each of these is reported below.

2.2.1 Evaluation of Surface Activity

Rhodium, platinum, nickel, ruthenium, palladium, and rhenium were studied as possible surface active metals in the diffusion bonding of tungsten single lap joints. These metals were plated on tungsten from commercially available "brush plating" electrolytic solutions. Because of the difficulty in plating a given metal thickness, no specific amount of material was plated on the tungsten. Instead, the plating variables were adjusted to give a continuous bright metallic plate on the tungsten surface, with the usual thickness being on the order of 5 x 10^{-5} inch.

The diffusion bonded single lap joints were evaluated by room temperature tensile tests and by joint remelt tests to 3200 F under a 15 psi load. The results of these tests are shown in Table I. Strong joints resulted when nickel, palladium, platinum, and rhodium were used as surface active metals. Rhenium is only marginally surface active, and ruthenium is apparently not surface active.

TABLE I

EVALUATION OF SURFACE ACTIVE METALS FOR BONDING TUNGSTEN

Metal	Room Temperature Tensile Shear		Remelt Temperatures (F)
	Number of Specimens	Average Breaking Load	
Pd	3	170	3200
Pt	3	143	3200
Ru	2	0	Not tested
Rh	3	182	Not tested
Re	3	39	Not tested
Ni	3	176	2750

Parent Material: 0.010 in. tungsten

Interfacial Materials: Pd, Pt, Ru, Rh, Re, or Ni (less than 0.0001 in. plate)

Joint Type: Single lap

Joint Area: 0.050 in. x 0.45 in.

Heating Time: 390 sec.

Pressure: 20,000 psi

Pressure Dwell: 60 sec (from 330 to 390 sec)

Atmosphere: Hydrogen

A tungsten to tungsten self-bond cannot be made under the conditions used in this study. Thus, the joint strengths obtained are assumed to result entirely from the use of metallic surface films.

From the results of this study, it can be concluded that palladium, platinum, and rhodium should be studied further in Phase II. Nickel should be eliminated because of its separation characteristics at 2750 F, and rhenium and ruthenium should be eliminated because of marginal surface activity.

2.2.? Diffusion Aids

By analogy, with the use of beryllium films on nickel for diffusion bonding superalloys (Ref. 5), boron on tantalum was selected for the bonding of refractory metals. Phase diagrams showed that only tantalum had any appreciable solubility for boron. Therefore, the boron diffusion aid would be in solid solution in tantalum after the joint was made. This procedure was necessary to avoid a layer of brittle boride at the joint interface. Accordingly, the system chosen for the evaluation of this concept was 90 Ta-10 W alloy bonded by an intermediate tantalum foil with boron on the surface.

Small quantities of boron were required and evaporation was selected to coat the tantalum foil (0.001 inch thickness). A vacuum evaporation apparatus was set up with a heater of 0.012 inch 90Ta-10W alloy strip. A dimple in this strip contained the boron. A variable transformer allowed the temperature to be controlled closely up to approximately 4200 F. The evaporation time was between two and four minutes. Longer times were not possible because of eventual failure of the heater. The boron films were thin and exhibited interference colors.

A bonding cycle of 5000 psi at 2000 F for 60 seconds gave double lap shear strengths of 135 pounds for 0.012 inch 90Ta-10W foil joined by 0.001 inch tantalum foil at the interface. These bonding conditions are not optimum for joining 90Ta-10W alloy, but if boron activates the process this would be readily apparent in higher strength values. When the boron-coated tantalum foil was substituted, the strengths fell to very low values. Hence, it was concluded that boron was not a diffusion aid in this system.

A second method was used to determine if boron was beneficial. In this method, the boron was ground to -325 mesh and applied as an acetone-base slurry. Again, no bond was obtained even after increasing the bonding pressure to 20,000 psi. It was concluded that boron was not a diffusion aid. One reason for this result may be that an interface of high melting TaB_2 is formed (melting point 5700 F) and in the short bonding time available, the solid solution is not formed.

2.2.3 Effect of Cold Work

This concept was evaluated with molybdenum double lap joints prepared with intermediate tantalum, columbium, and vanadium foils. The foils were used in the cold worked and recrystallized conditions. Although the original study was to be limited to the use of tantalum foils, columbium and vanadium were included to confirm the results obtained with tantalum.

The recrystallization behavior of the 0.001 inch tantalum foil was determined at the beginning of the study so that later joint failure data could be correlated to this behavior. A five-minute anneal at temperatures ranging from 1450 to 2400 F was performed on microtensile specimens. The results are shown in Figure 1. Recrystallization is not quite complete at 2000 F as indicated by the retention of some small part of the strengthening due to cold work. Hence, typical bonding cycles at 2000 F will be accompanied by partial recrystallization.

Preliminary bonding studies at 2000 F and 15,000 psi indicated good joints were formed at bonding times ranging from 5 to 60 seconds.

Double lap joints were made having a total lap area of 0.1 square inch (2-0.4 in. x 0.125 in.). The results are shown in Figure 2. In all cases, a sound joint was made, and failure occurred in the TZM foils.

To study bonding characteristics, failure must be forced into the joint. Failure was investigated by bonding at a constant time of 60 seconds at progressively lower pressures. Joints made with cold worked tantalum were compared with joints made with fully recrystallized (2400 F, 5 min) tantalum. Figure 3 shows that only at low bonding pressures does failure begin to occur solely in the lap area and that at intermediate pressures, failure occurs in both the TZM and the lap. At higher bonding pressures, the TZM failed near its tensile strength. Figure 4 shows that the stress attained in the TZM foil is high enough to cause plastic flow and necking.

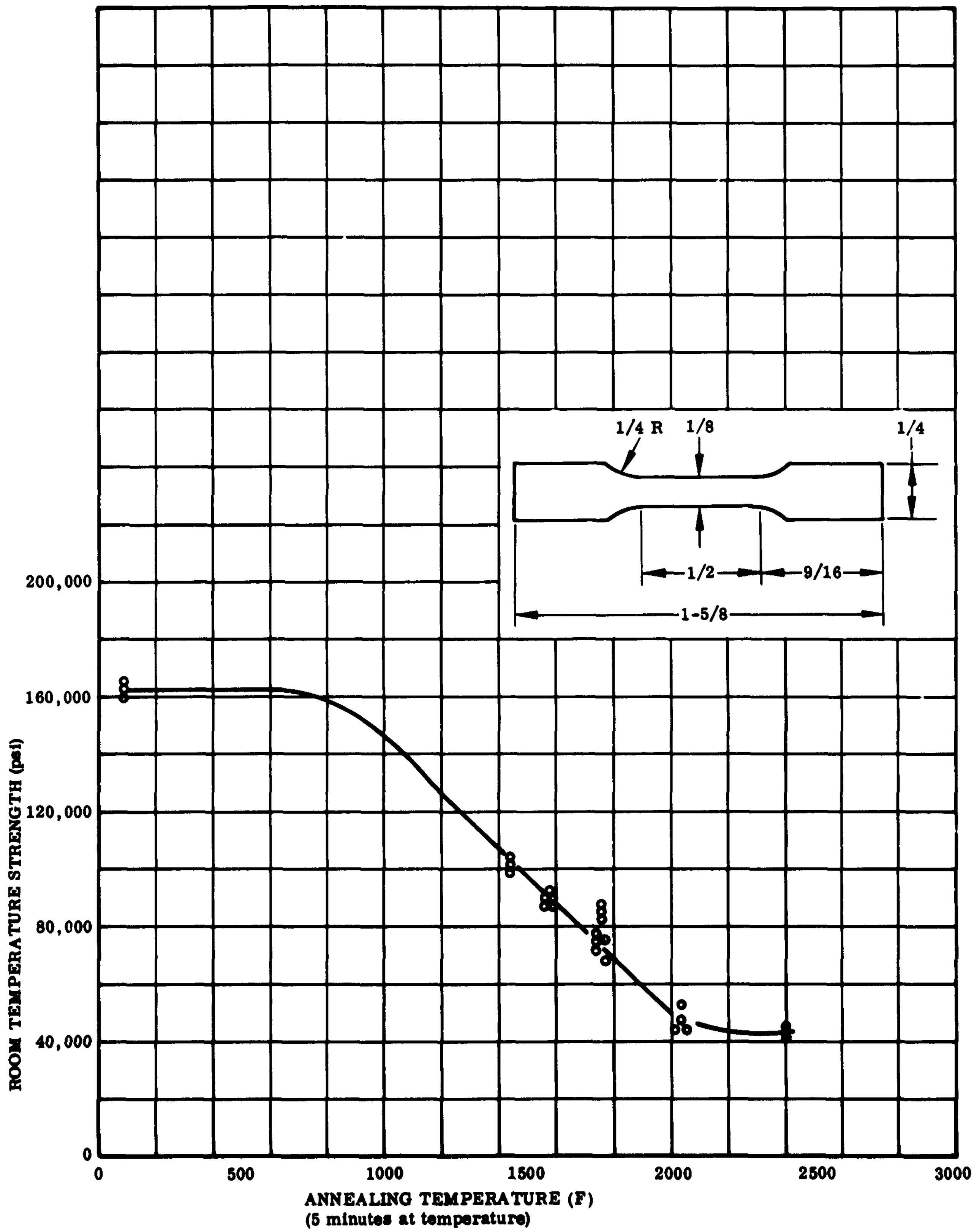


FIGURE 1. ROOM TEMPERATURE STRENGTH OF 0.001-INCH TANTALUM FOIL.

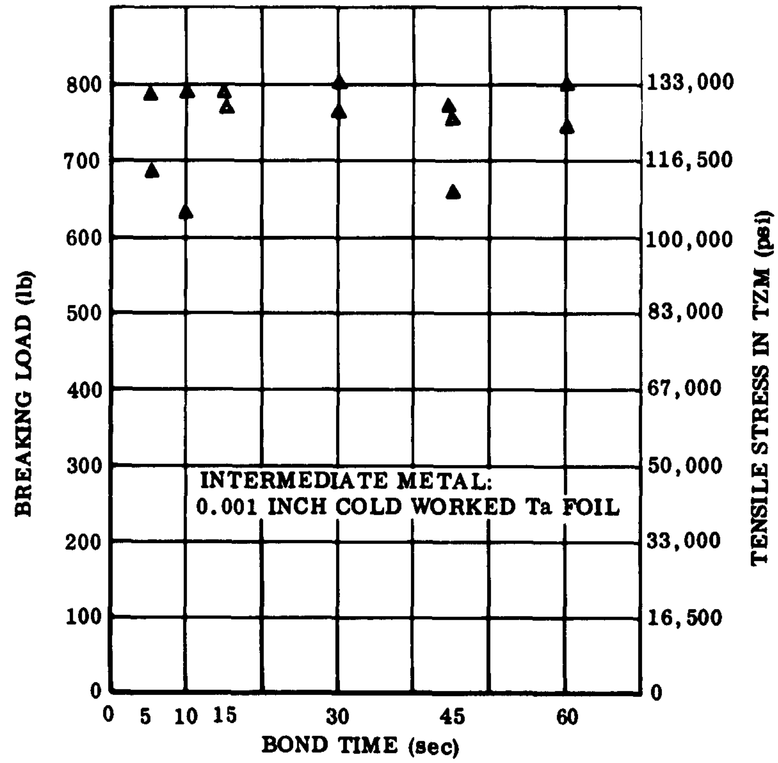


FIGURE 2. STRENGTH OF DOUBLE LAP SHEAR JOINTS IN 0.012-INCH TZM BONDED AT 2000 F UNDER 15,000 PSI

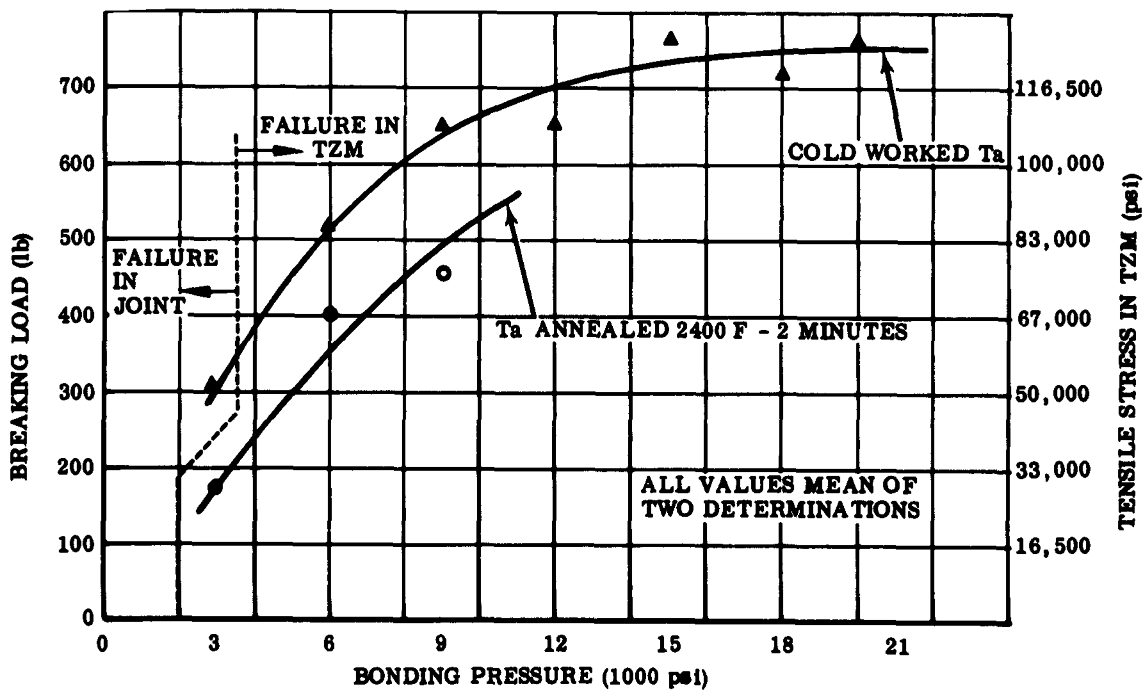
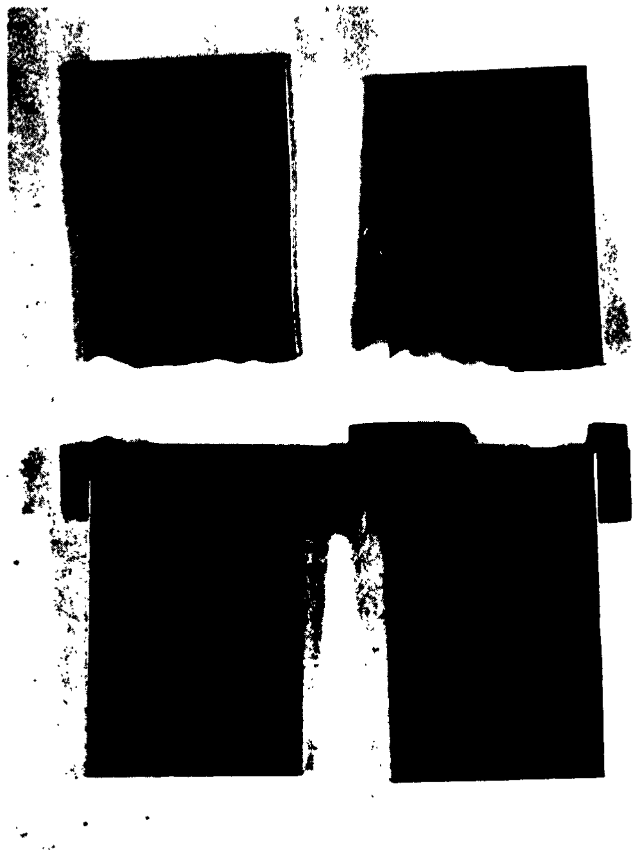


FIGURE 3. STRENGTH OF DOUBLE LAP SHEAR JOINTS IN 0.012-INCH TZM BONDED AT 2000 F FOR 60 SECONDS



TZM bonded with 0.001 inch tantalum foil at 2000 F under 6000 psi for 60 seconds. Note deformation in TZM at failure in upper half of specimen (single thickness).

Excess tantalum foil has not been trimmed from this specimen.

FIGURE 4. DOUBLE LAP SHEAR TEST SPECIMEN

The results shown in Figure 3 were not regarded to be a clean cut demonstration that the cold work in the tantalum foil promoted recrystallization and hence, bonding. The lower strength values could have been the result of slight surface contamination from annealing, even though precautions were taken to prevent contamination. In the later studies performed with columbium foil, the opposite effect was noted with use of the annealed foil resulting in higher joint strengths (Fig. 6).

After the preliminary studies, in which time and pressure were varied, the effect of bonding temperature variation was studied bwtween 1800 and 2200 F. The heating cycle was standardized at 390 seconds from furnace start to the end of the bonding cycle, and the joint area was reduced to 0.045 square inch (2 lap areas each 0.45 x 0.050 in.) to ensure greater possibility of joint failure during testing.

Table II and Figure 5 present the results of the study. As a result of the thermal cycle during the bonding process, the tantalum foil was either partially annealed to varying degrees or was fully recrystallized. The tantalum annealing curve of Figure 1 illustrates that recrystallization is nearly complete at 2000 F. At bonding temperatures higher than 2000 F the tantalum is fully recrystallized, whereas at temperatures below 2000 F much less recrystallization takes place in the foil. The portion of the curve in Figure 5 representing the fully annealed tantalum foil (i.e., the points at 2100 and 2200 F) has been extrapolated to 2000 F to give a strength value representative of foil fully annealed prior to application of pressure. The actual 2000 F strength is higher. This is believed to result from recrystallization of the tantalum foil during bonding. In other words, there appears to be an increase in strength attributable directly to bonding at the recrystallization temperature.

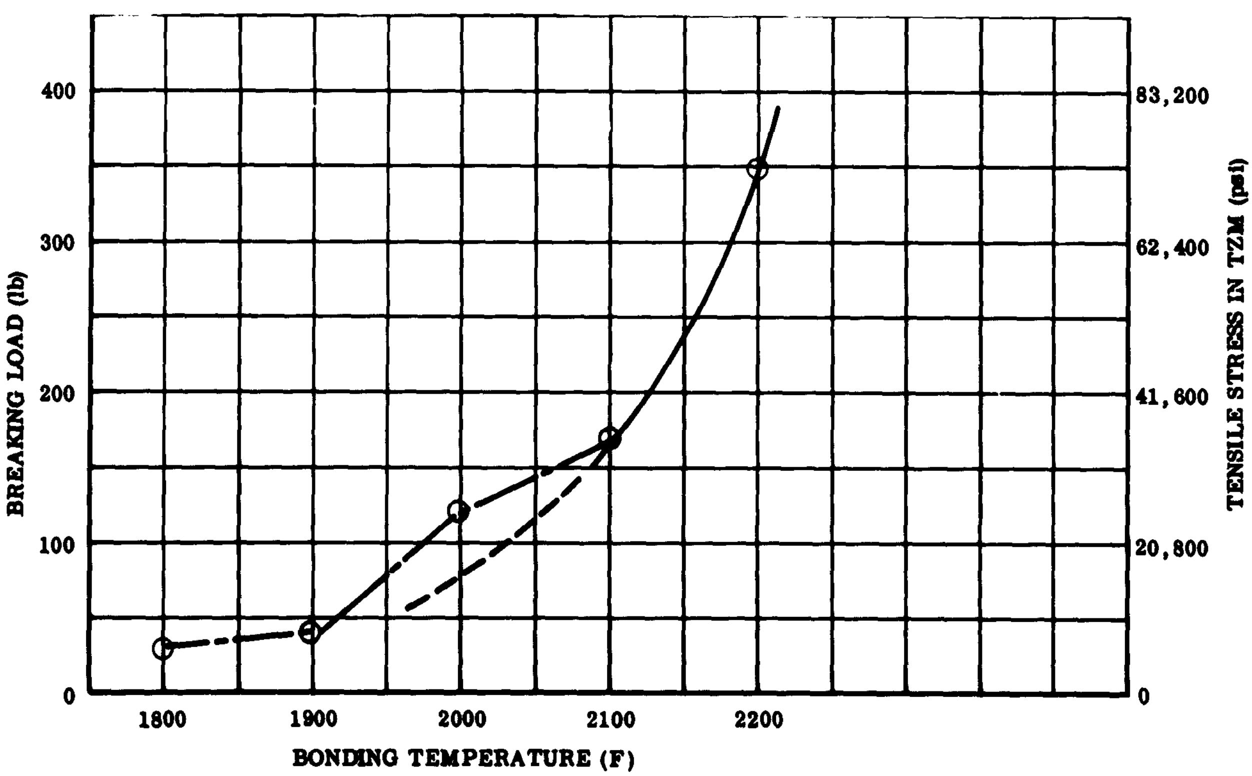


FIGURE 5. STRENGTH OF DOUBLE LAP TZM-Ta JOINTS

TABLE II

SUMMARY OF RESULTS ON TZM BONDED WITH TANTALUM FOIL

Temperature (F)	Number of Specimens	Percent Tensile Failures	Percent Shear Failures	Average Breaking Load (lb)	Standard Deviation (lb)	Coefficient of Variation (%)
Cold worked Ta						
1800	3	0	100	28	27	96
1900	3	0	100	43	8	20
2000	3	100	0	115	4	3
2100	3	100	0	170	0	0
2200	3	100	0	340	82	24
Annealed Ta, same conditions of bonding. Annealed for 2 min at 2400 F.						
2000	3	67	33	166	65	39

Total Specimens: 18

Parent Material: 0.012 in. TZM

Interfacial Material: 0.001 in. Ta

Joint Type: Double lap

Joint Area: 2 - 0.050 in. x 0.40 in.

Heating Time: 390 sec

Pressure: 12,000 psi

Pressure Dwell: 60 sec (from 330 to 390 sec)

TABLE III

SUMMARY OF RESULTS ON TZM BONDED WITH COLUMBIUM FOIL

Temperature (F)	Number of Specimens	Percent Tensile Failures	Average Breaking Load (lb)	Standard Deviation (lb)	Coefficient of Variation (%)
		Cold worked Cb foil.			
1700	4	25	121	39	32
1800	5	80	230	86	37
1900	10	100	305	98	32
2000	6	100	272	115	42
2100	10	100	341	106	31
2200	6	100	376	128	34
2300	4	100	482	47	10
Total Specimens: 45					
		As above, but Cb annealed 20 mins at 2300 F.			
1800	4	75	277	49	18
1900	7	100	341	64	19
2000	6	100	367	76	21
2100	3	100	449	59	12
2200	3	100	542	27	5
Total Specimens: 23					

Parent Material: 0.012 in. TZM

Interfacial Material: 0.001 in. Cb

Joint Type: Double lap

Joint Area: 2 - 0.050 in. x 0.45 in.

Heating Time: 390 sec

Pressure: 12,000 psi

Pressure Dwell: 60 sec (from 330 to 390 sec)

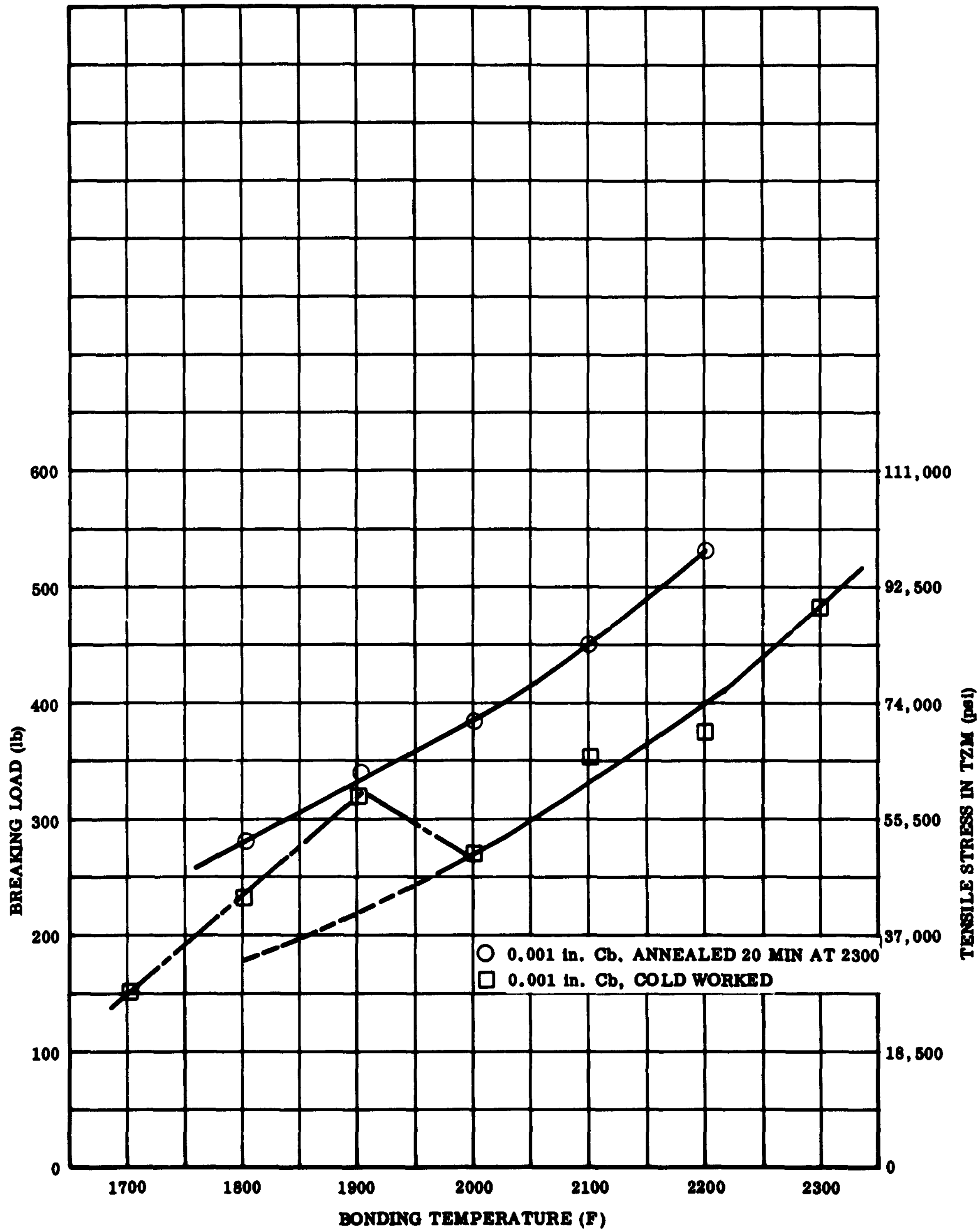


FIGURE 6. STRENGTH OF DOUBLE LAP TZM-Cb JOINTS

To confirm this observed effect, similar joints were made with columbium and vanadium foil. Up to ten specimens were made under a given set of conditions to give the results adequate significance. The results for columbium and vanadium are shown in Figures 6 and 7. The data are summarized in Tables III and IV. The scatter in the results is larger than desired for the data, but failure was purposely forced into the joint, with consequent lower reproducibility. Surface roughness and other physical characteristics of the TZM sheets used in the program vary which results in additional cause for scatter.

A bonding study with annealed columbium foil (2300 F, 20 min) was also performed and is shown in the data summarizations. The strength of these joints was higher than the joints made with cold worked foil. The result with columbium is contrary to the results with tantalum, but the series with annealed columbium foil was made at a different time, with a different sheet of TZM, so that direct comparison is not appropriate. However, the annealed columbium joints did not have the 1900 F strength peak exhibited by the cold worked columbium foil joints.

The columbium and vanadium studies confirmed the results of the tantalum study. The strength results at 1900 F for columbium and 1600 to 1700 F for vanadian were about one standard deviation above the extrapolated strength values for fully recrystallized foils. Although a question may be raised regarding the extrapolation of the curves, it nevertheless follows the general trend of values expected from fully annealed foils.

On the basis of the work performed in the study of this concept, the following conclusions may be drawn:

1) Recrystallization of the intermediate foil during the application of bonding pressures results in an increase in joint strength over that realized from bonding with fully recrystallized foil.

2) The advantages of bonding under conditions of recrystallization are small, and can be equalled by increasing the bond temperature by 50 to 150 F.

2.2.4 Effect of Induction Heating

This concept appeared to offer the possibility of speeding up diffusion bonding because of claims (Ref. 6) that an increase of up to ten times in the diffusion rate had been realized by high frequency heating (700 kc frequency). A program was planned

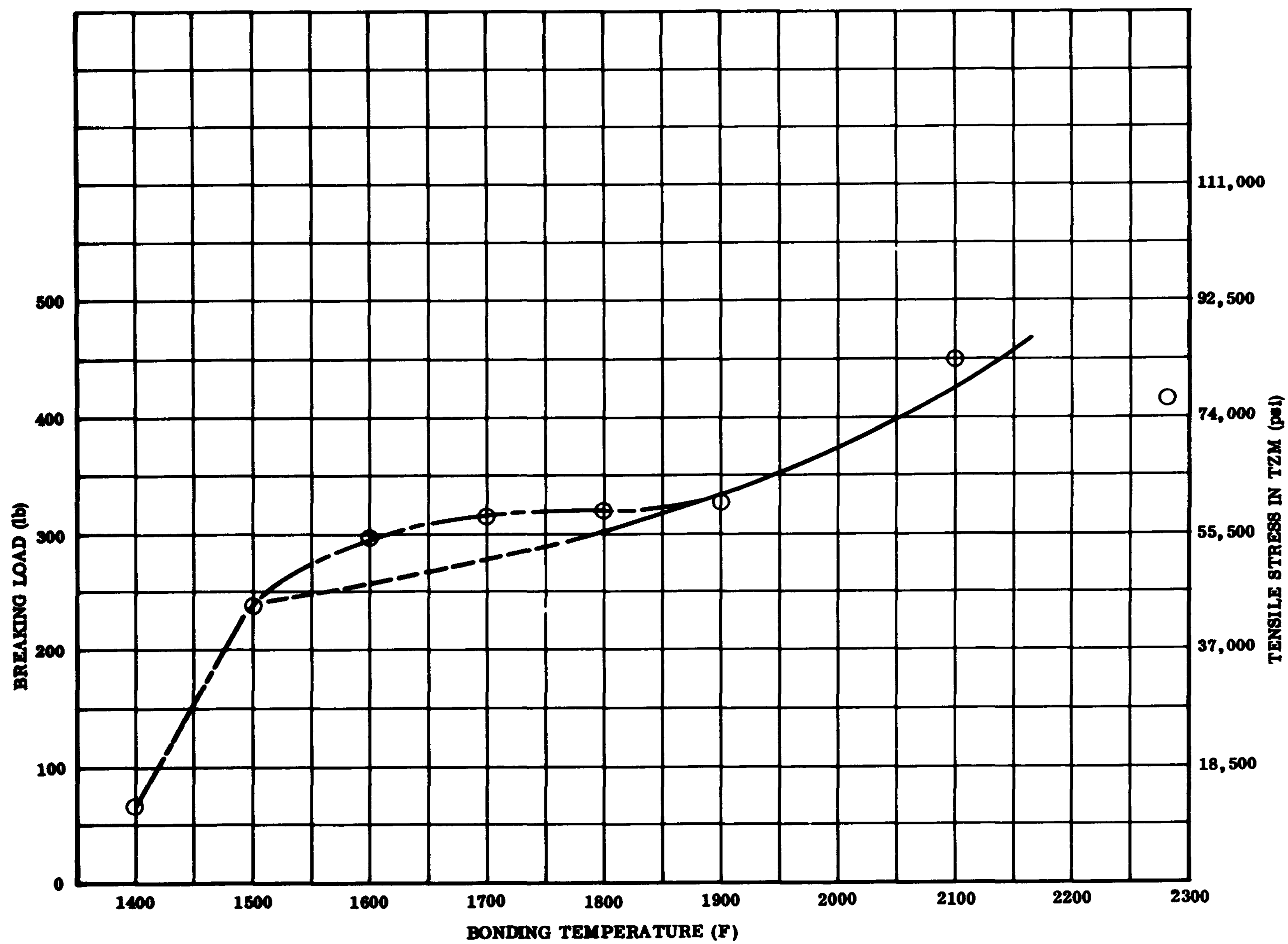


FIGURE 7. STRENGTH OF DOUBLE LAP TZM-V JOINTS

TABLE IV

SUMMARY OF RESULTS ON TZM BONDED WITH VANADIUM FOIL

Temperature (F)	Number of Specimens	Percent Tensile Failures	Average Breaking Load (lb)	Standard Deviation (lb)	Coefficient of Variation (%)
1400	3	0	68	33	48
1500	8	87	241	49	20
1600	5	100	296	29	10
1700	10	100	313	74	24
1800	3	100	313	54	17
1900	7	86	325	60	18
2100	6	100	449	120	27
2300	5	100	416	130	31

Parent Material: 0.012 in. TZM

Interfacial Material: 0.001 in. V cold worked

Joint Type: Double lap

Joint Area: 2 - 0.050 in. x 0.45 in.

Heating Time: 390 sec

Pressure: 12,000 psi

Pressure Dwell: 60 sec (from 330 to 390 sec)

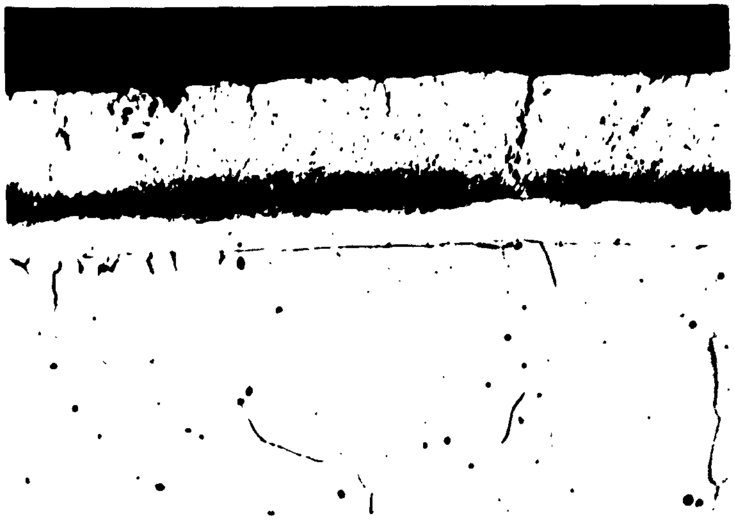


FIGURE 8.

Magnification: X250

Etched: Nital + Electrolytic NaOH

Heated 10 minutes in resistance furnace.

DIFFUSION OF CHROMIUM INTO IRON

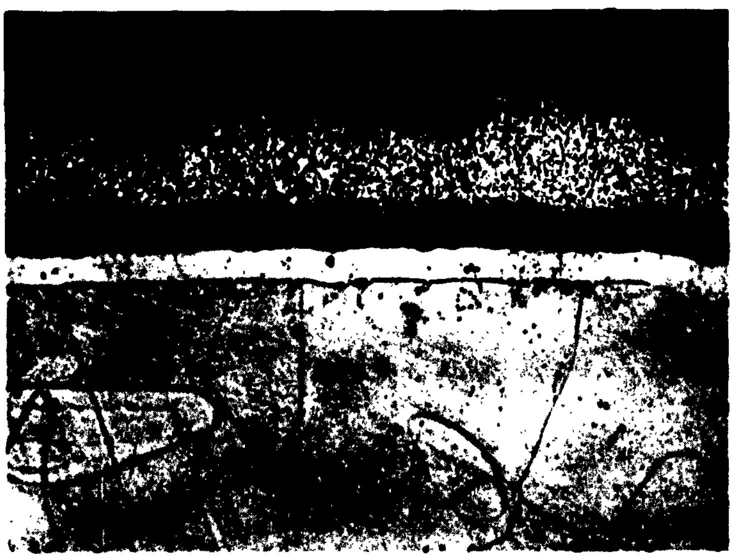


FIGURE 9.

Magnification: X250

Etched: Nital + Electrolytic NaOH

Heated 10 minutes in high frequency furnace.

to confirm the original results obtained with chromium diffusion into iron, and to extend it to chromium diffusion into nickel and molybdenum. The extension of the program was not started because the original claims could not be confirmed using 200 kc induction heating.

Because of the importance of temperature as a rate-controlling factor in diffusion, the method of temperature measurement received prime consideration in the design of the equipment for both induction and radiant heating. Armco iron specimens (1/2 in. diameter by 1/2 in. long) plated with two mils of chromium were heated in a vacuum bell jar furnace by one of two methods: (1) by thermal radiation from a resistance heated (60 cycle ac) molybdenum tube, and (2) by direct inducting coupling with a concentration type work coil. The temperature was measured with a calibrated optical pyrometer by sighting into a black body cavity in the end of the specimens, thus ensuring directly comparable temperatures for all specimens regardless of heating method.

Figures 8 through 11 are photomicrographs of specimens heated either by induction or radiant methods at 2000 F for periods of 10 and 30 minutes. The heating method appears to have no effect on the rate of diffusion as determined by the average thickness of the diffusion layer between the chromium plate and the iron core. Figure 12 shows the microstructure of a plated specimen prior to diffusion treatment.

A plot of these data, assuming the parabolic relationship $x^2 = 4Dt$ to be valid, is shown in Figure 13. The uncertainty of diffusion layer thickness measurement can result in a superposition of the curves for each heating method. The diffusion coefficient (D) is taken to be the slope of the straight line plot and the average experimental value is $0.12 \times 10^{-8} cm^2/sec$.

The values claimed by Samuel range from 0.21 to $1.36 \times 10^{-8} cm^2/sec$ at 1100 C (2012 F). Careful examination of these claims reveals that the high diffusion rate occurred only in solid-solid diffusion where the specimen was immersed in an alumina-chromium pack. Samuel stated this pack was observed to heat in the absence of the specimen. Suspicion that the pack heating affects the results was confirmed by data for different sized packs surrounding the specimen, and the existence of diffusion layer thicknesses at so-called zero time. The author claims that high frequency fields increase the diffusion rate. This should be modified to claim that the combined action of a high frequency field and the special chromizing pack cause the observed effect. The experiments at Solar were conducted in hydrogen to isolate the high frequency effect when no increase was found in the diffusion rate depending on the heating method.
depending on the heating method.

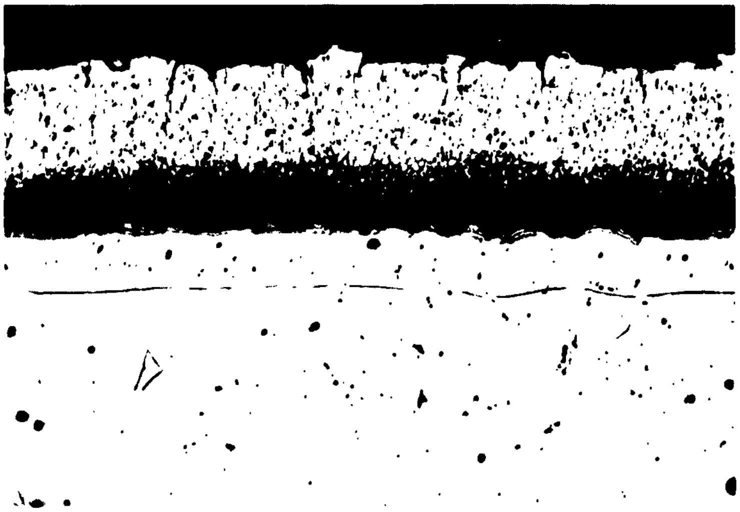


FIGURE 10.

Magnification: X250

Etched: Nital + Electrolytic NaOH

Heated 30 minutes in resistance furnace.

DIFFUSION OF CHROMIUM INTO IRON

FIGURE 11.

Magnification: X250

Etched: Nital + Electrolytic NaOH

Heated 30 minutes in high frequency furnace.

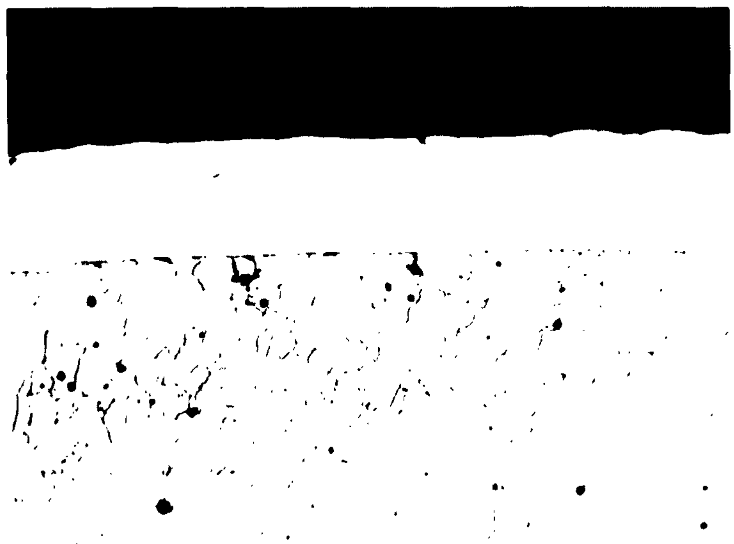


FIGURE 12. ARMCO IRON AS PLATED WITH CHROMIUM

Magnification: X250

Etched: Nital

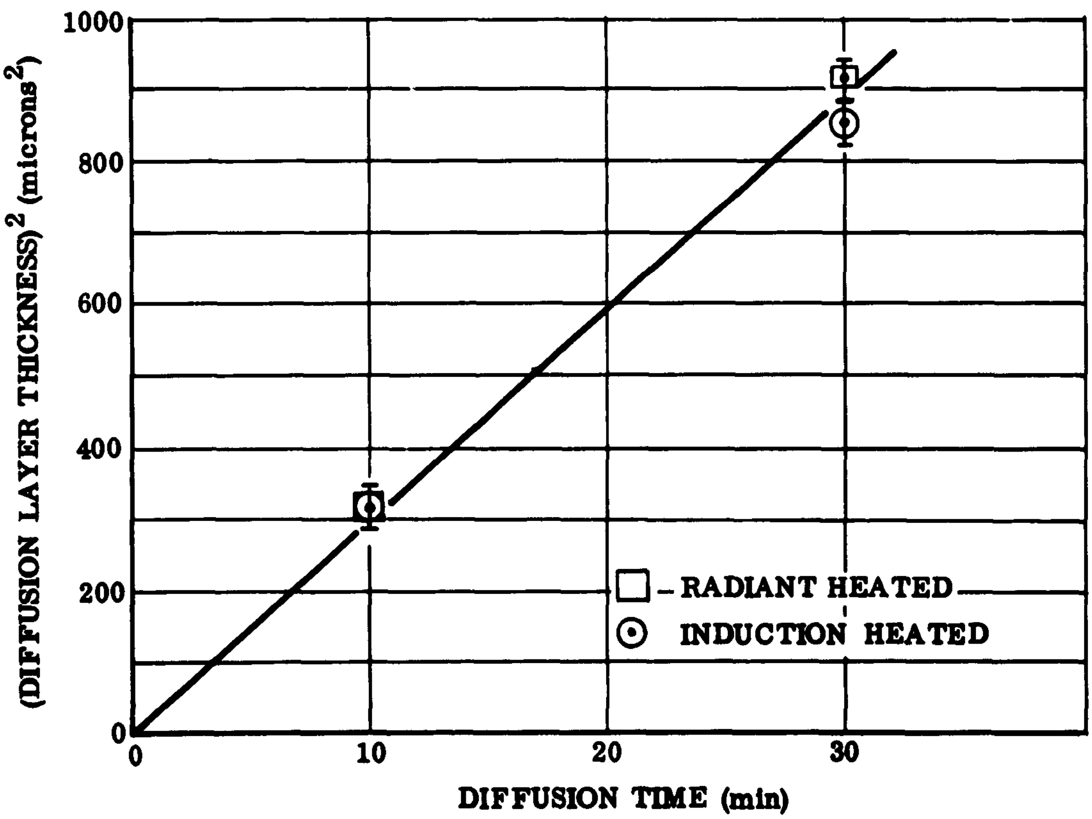
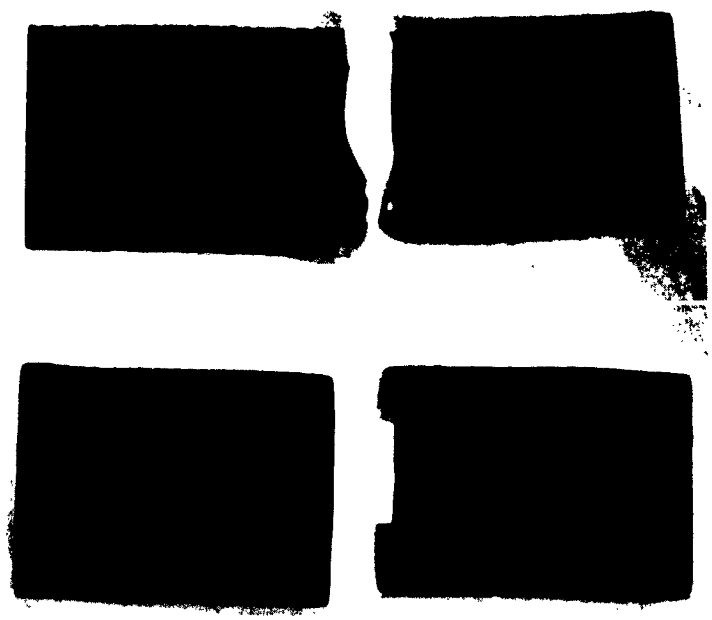


FIGURE 13. DIFFUSION LAYER GROWTH VS TIME FOR CHROMIUM INTO IRON AT 2000 F

2.2.5 Allotropic Transformation Effects

In the evaluation of this concept titanium foil was used as the allotropically transforming intermediate material and TZM or D36 as the alloy to be joined. Bond temperatures ranging between 1425 and 1825 F were selected so that bonds could be made at temperatures which would encompass the titanium transformation at approximately 1620 F. Double lap joints were made and the strength of the joints was determined at room temperature with a Hounsfield tensiometer.

The D36 alloy had originally been selected for the performance of this study and single lap joints were made with an intermediate of one thickness of 0.3 mil titanium. Bonds were made at 1570 F and 3,000 psi in 30 seconds. Subsequent testing of these joints resulted in failure in the six mil D36 in all cases (Fig. 14). It was necessary to obtain joint failure to determine any effects caused by the transformation. Since it was impractical to reduce the joint area, and no thicker D36 was available at the time, 12 mil TZM was substituted for the D36.



Bonded with titanium foil at 1570 F for 30 seconds under 3000 psi.
Failure occurs in D36 in each case.

FIGURE 14. DOUBLE LAP SHEAR SPECIMEN OF D36

Two series of tests were performed with the TZM-Ti system. The results of these tests are shown in Figure 15 and Table V. The difference in strength results, between the two series of tests, is apparently caused by the difference in bond areas used in the two series. However, this difference did not affect the validity of the tests.

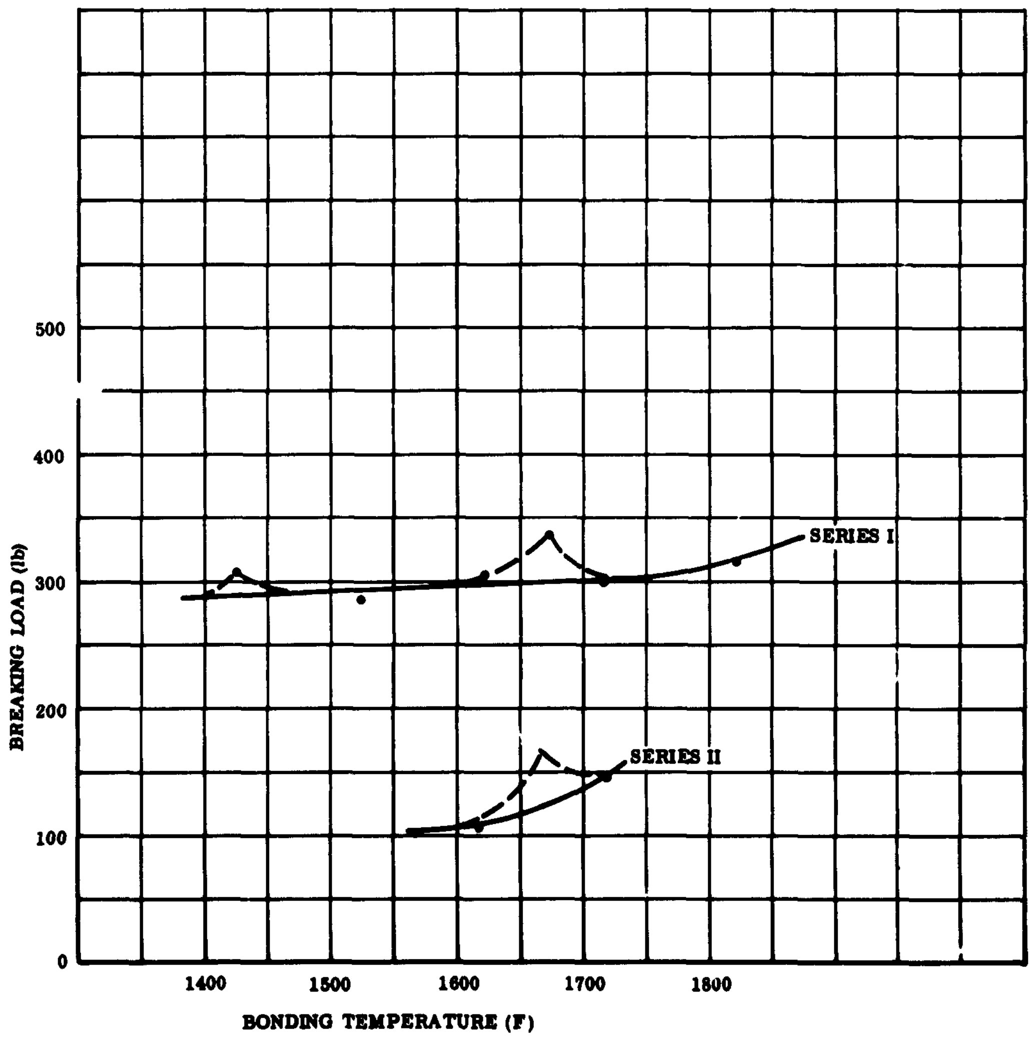


FIGURE 15. STRENGTH OF TZM-Ti DOUBLE LAP JOINTS

TABLE V

SUMMARY OF RESULTS ON TZM BONDED WITH TITANIUM FOIL

Temperature (F)	Number of Specimens	Percent Tensile Failures	Average Breaking Load (lb)	Standard Deviation (lb)	Coefficient of Variation (%)
SERIES I					
1425	3	67	305	67	22
1525	3	100	288	66	23
1625	5	100	306	46	15
1675	5	100	335	24	7
1725	4	100	300	17	6
1825	3	100	318	16	5
Parent Material: 0.012 in. TZM Interfacial Material: 0.0003 in. Ti (cold worked) (three thicknesses) Joint Type: Double lap Joint Area: 2 - 0.050 in. x 0.45 in. Heating Time: 390 sec Pressure: 12,000 psi Pressure Dwell: 60 sec (from 330 to 390 sec) Atmosphere: Ti gettered A					
SERIES II					
1570	5	40	100	35	35
1620	4	25	108	34	32
1670	4	50	164	19	11
1720	5	100	146	30	21
Same as for Series I, except: Interfacial Material: 0.0003 in. Ti (cold worked) (one thickness) Joint Area: 2 - 0.125 in. x 0.0625 in. Pressure: 10,000 psi					

The allotropic transformation in pure titanium occurs at 1625 F, but the original (Series II) data obtained in this program indicated that an increase in bond strength occurred at a bond temperature of 1670 F. An examination of the Ti-O and Ti-N constitution diagrams indicated that as little as seven micrograms of either gas in the titanium used in the bond area could result in the transformation being raised from 1625 to 1675 F. It was, therefore, felt that the effect observed at 1670 F resulted from the allotropic transformation.

A second series of tests (Series I) was then performed to confirm the original results. The temperature range of investigation was extended to ensure the inclusion of any transformation effects which may have fallen outside of the original temperature range. Also, three thicknesses of 0.3 mil titanium foil were used in the joint so that the results obtained could be more directly compared with those of other types of joints prepared with one mil foils.

The Series I results confirmed the strength peak at about 1675 F, and, in addition, indicated a possible peak at 1425 F. This latter peak was probably caused by the recrystallization of the titanium foil during bonding and is identical to the effect studied in Concept 3. The increase in strength at the allotropic transformation (1675 F) is not very significant, since it increases the strength of the joint only 14 percent.

A slight increase in joint strength occurs at the allotropic transformation temperature of titanium. This increase may be caused by a superplasticity effect which may occur during the transformation, as discussed in Section 2.1. The increase would result in more complete mating of the titanium with the TZM surface, thus increasing the bond strength.

2.2.6 Subsolidus intermediate metals

The Zr-4.5 Cr alloy has a solidus temperature of 1300 C (2370 F), and is compatible metallurgically with columbium. In this study 0.14 mil zirconium foil was electroplated with sufficient chromium to give a Zr-4.5 Cr alloy after a diffusion treatment. It was expected that bonding near the solidus temperature of this alloy would result in a substantial reduction of the required bonding pressure.

TABLE VI

RESULTS OF SUBSOLIDUS INTERMEDIATE METALS STUDY

	Temperature (F)	Bonding Pressure (psi)	Number of Specimens	Average Breaking Load (lb)
Interfacial material: 0.14 mil zirconium - 4.5% chromium alloy	2000	5000	3	406
	2200	5000	1	405
	2200	1000	1	460
Interfacial material: None (self-bond)	2000	3000	1	90
Interfacial material: Tin plate on D36	2000	3000	1	0
Interfacial material: Tin plate on copper plate on D36	2000	1000	1	224
Interfacial material: Copper plate on D36	2000	3000	2	290
	2000	3000	2	Joints melted at 1825 F under 15 psi load. Possibly hot short.

Parent Material: 0.012 in. D36

Joint Type: Double lap

Joint Area: 2 - 0.050 in. x 0.45 in.

Heating Line: 390 sec

Pressure Dwell: 60 sec (from 330 to 390 sec)

Bonding of the D36 with the alloy foil resulted in strong joints, and failure occurred in the D36 under all bonding conditions. Since it was impractical to adjust the joint area to give joint failure, this course of study was abandoned and the columbium tin system was studied.

The solubility of tin in columbium is approximately 10 percent. The system has only one intermetallic compound, and below 30 percent tin there are no liquid phases below 3600 F. Although the tin would be liquid at the anticipated bonding temperatures, subsequent diffusion during bonding was expected to remove the liquid phases. Tin was plated on the D36 and although the plate was poor, a sufficient coating of tin was obtained to perform the experiments. The use of tin as an intermediate did not result in a bond.

To substantiate these results, tin was plated over a copper flash since copper plated rather well on the D36, and tin plated well on the copper. Fairly good bond strength was obtained, but subsequent tests with copper alone indicated that the copper caused the observed joint strengths.

The D36-Cu combination was developed further to see what merit it may have had, since no constitution diagram was available on which to predict possible results. Elevated temperature separation tests, under a 15 psi shear load in the joint, resulted in separation of the joint at about 1825 F. There were also indications that diffusion of copper into the D36 produced hot short properties in the D36. Thus, this system was also abandoned. The results of these investigations are shown in Table VI.

In conclusion, the lack of systems metallurgically compatible with columbium will prevent complete evaluation of this concept. The difficulties of control in such systems, e.g., W-Ni-W, to prevent failure at intermediate temperatures has led to a decision to abandon this approach.

2.3 DISCUSSION OF RESULTS

The purpose of this work has been to uncover methods to activate the diffusion bonding process. Six concepts have been tested with the results reported earlier. In summary these results are:

Concept 1.- Use of surface active elements. Nickel, platinum, palladium, and rhodium permit rapid bonding of tungsten under conditions where no bonding occurs in the absence of these metals. Ruthenium and rhenium are not effective. These four metals will be used for bonding tungsten in Phase II.

Concept 2.- Use of diffusion aids. Boron coatings on tantalum were selected to investigate this concept. Results showed that this system did not accelerate bonding and no further work is planned in Phase II.

Concept 3. Effect of cold work. When recrystallization occurs during the bonding process, enhanced bond strengths result. The effect is small, and it is not planned to exploit this effect in Phase II work.

Concept 4. Effect of induction heating on diffusion rate. This effect which was claimed to cause up to tenfold increase in diffusion rate could not be confirmed.

Concept 5. Effect of allotropic transformation. A small effect has been found at the allotropic transformation of titanium, but it is too small for practical use. Certain theoretical studies on superplasticity suggest ways to enhance the effect, and these will be investigated in Phase II.

Concept 6. Subsolidus effects. It has not been possible to find entirely suitable systems to exploit this effect, and no further work is planned in Phase II.

The work on the evaluation of concepts showed other problems in these diffusion bonded joints. The major problem revealed has been the poor performance in "peel". This term is used in the same sense as in the adhesive bonding field and implies resistance to the application of a torque about the line of the joint. It must be emphasized that non-optimum conditions have had to be used throughout the concept evaluation work to avoid testing the foils instead of the joint. An overlap of 0.050 inch appears to be the minimum that can be used, but to force failure into the joint the shear strength of the bond must be less than one eighth that of the foil (0.012-inch). Certain evidence suggests that the strength of optimum diffusion bond is low when a stress is applied normal to the bond, although the bond may have sufficient strength in shear to cause typical tensile failures of the refractory metal foil. This problem will be examined in more detail in Phase II of the program.

III. WORK ON PHASE II - PRINCIPAL FABRICATION EFFORT

The work in this phase will lead to the development of diffusion bonding processes for the refractory metals. Major efforts will be applied to several tasks:

1. Joint Design. A survey of refractory metal structures has been made and joint designs are based on this survey.

2. Development of Tooling. Included in this task will be an experimenta study of tooling parameters as well as the design and construction of tooling.

3. Selection and Properties of Alloys. Base line data will be gathered on the properties of selected refractory alloys.

4. Bonding Investigation. The development of bonding processes will be accomplished in this task.

5. Coating Investigation. Some of the factors to be included in this task are the relationship between coatings and joint design, the coating of joints, and the testing of coated joints.

6. Testing of Joints. Considerable test work will be performed in this program so that the selection of meaningful tests is extremely important. The significance of tests will be examined in this task.

3.1 JOINT DESIGN

One objective of the work being done on this program is the development of efficient joint configurations for high temperature structures through the use of diffusion bonding. To assure the development of a joint which will be representative of those required on future Air Force vehicles, a survey of trends in high temperature structural systems has been performed.

The survey of structural systems was conducted within the material limitations imposed by this contract. Specifically, the structures investigated must:

- Use refractory metals
- Operate between 2000 and 4000 F
- Use material gages from 0.006 to 0.012 inch

The structural requirements associated with various current Air Force systems were evaluated and compared with the capabilities of high temperature structures and materials. Structural systems which hold promise for future use were selected for further evaluation. Typical joint requirements were then selected from these structural systems.

3.1.1 Survey of Structural Systems for High Temperatures

Work in support of Dyna Soar, ASSET and Spaceplane was reviewed, as well as recent development programs in high temperature structures. The combination of temperature and material thickness parameters mentioned above eliminate all structures other than external surfaces on glide re-entry vehicles. The various approaches to the design of a high temperature metallic structure for a glide re-entry vehicle can be categorized as:

- Hot monocoque
- Radiation shields plus insulated, or insulated and cooled substructure

These approaches are illustrated below.

Hot Monocoque Structure

Hot monocoque structures are characterized by systems which employ the hot external surface as the load-carrying surface. Cooling is not used, and insulation behind the structure serves only to protect payload or fuel from excessive heating. Since the external surface must take all loads, this surface must be rigid. Relief of thermal stresses by floating panels and corrugations becomes difficult. Thermal stresses become severe as the maximum operating temperatures become higher and the system weight begins to climb. Therefore, if this system is to be competitive with other forms of hot structure, it will probably be used at the lower end of the high temperature range.

Structural systems falling into the hot monocoque category are exemplified by work conducted recently on two development programs.

- Refractory Metals Structural Development Program - AF33(616)6578 - McDonnell and General Electric
- Manufacturing Method and Design Procedures of Brazed Refractory Metal Honeycomb Sandwich Panels - AF33(657)7276 - Martin Marietta Corporation

McDonnell-General Electric Program. The use of skin-spar construction was investigated, leading to the design, fabricating, and testing of a typical fin-rudder section for an advanced vehicle. Calculated surface temperatures would approach 2500 F during re-entry. Final component substructure is shown in Figure 16. Typical skin panels are shown in Figure 17. Both columbium alloys (FS82 and F48) and molybdenum alloys (Mo-5Zr and TZM) were considered.

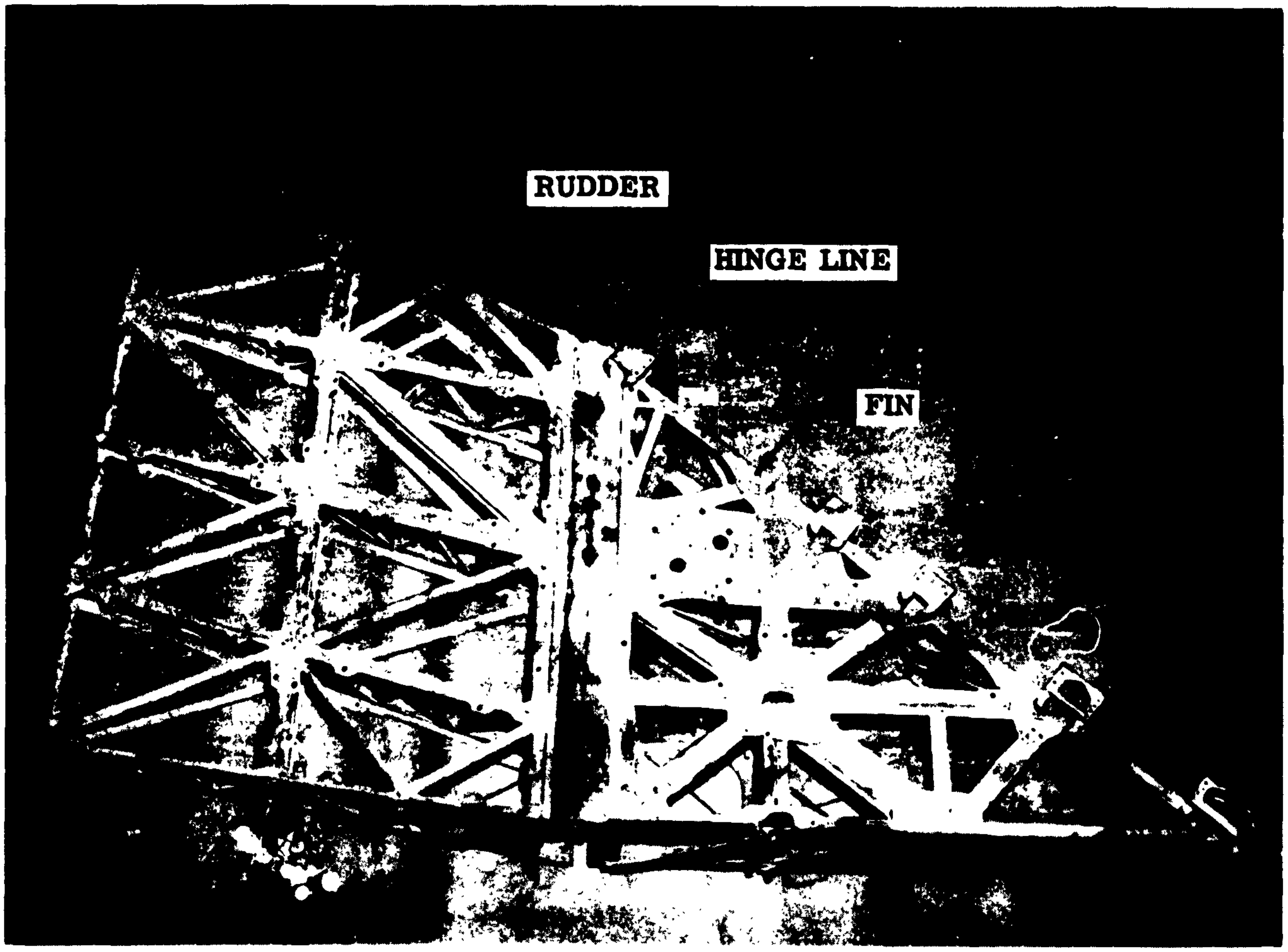


FIGURE 16. TYPICAL SUBSTRATE FOR REFRACTORY METAL HOT MONOCOQUE CONSTRUCTION

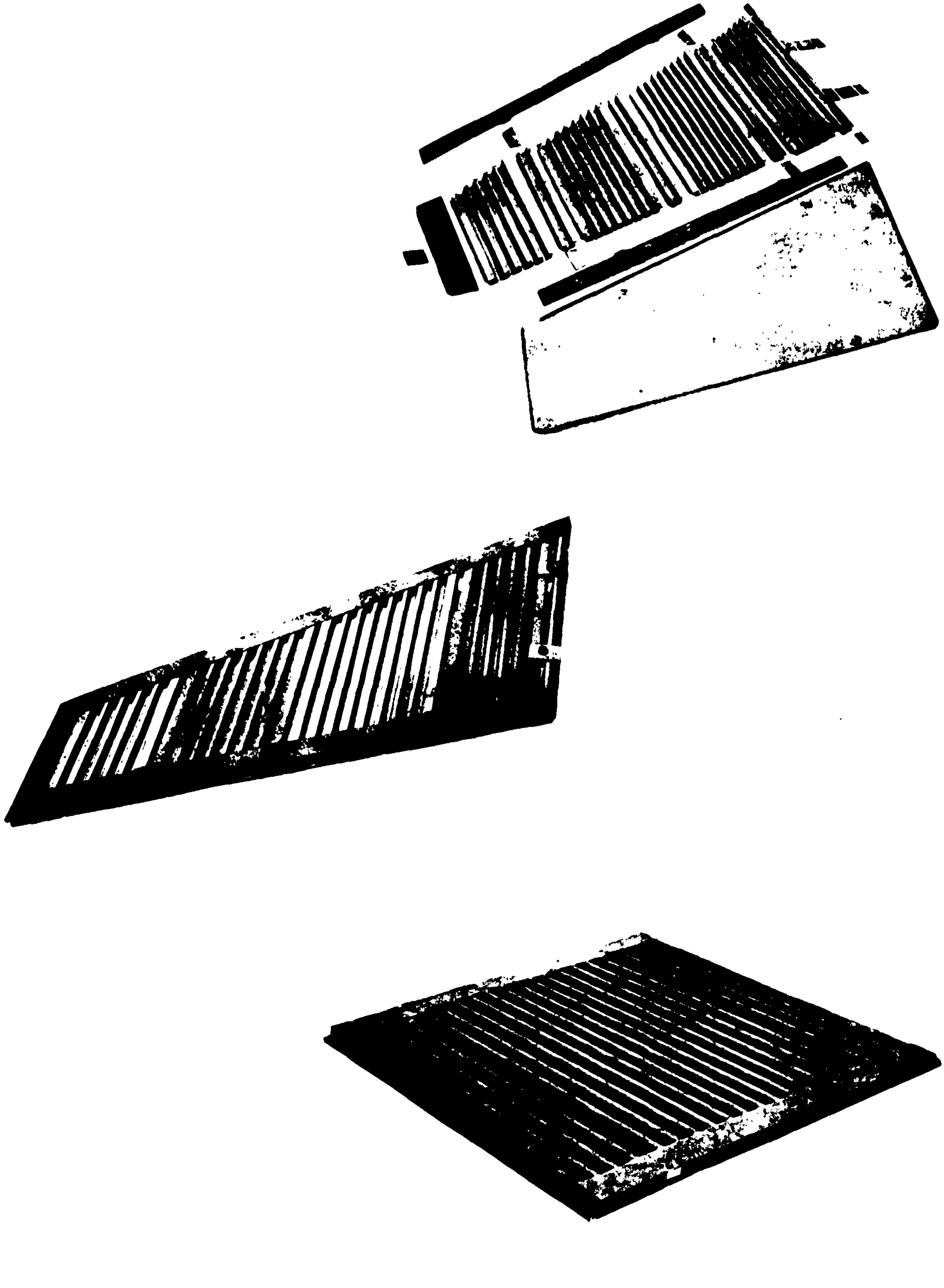


FIGURE 17. TYPICAL CORRUGATION-STIFFENED PANELS FOR REFRACTORY METAL HOT MONOCOQUE CONSTRUCTION

Various designs of rigid surface panels were considered, and all resulted in failures due to inability to accomodate thermal expansion. The final panels shown in Figure 17 were designed to accept mainly air pressure loads through corrugations, and all other loads were reacted mostly by substructure.

Various methods were evaluated for attaching the corrugated skin panels to the spar webs. Some of these are shown in Figure 18. The general arrangement of the corrugated spar-panel attachment is illustrated in Figure 19.

Joints which may be suitable for use of diffusion bonding are:

- Joint of corrugation to face sheet
- Joint of doubler to corrugation
- Joint of panels to spar cap
- Joint of corrugated spar web to spar cap

Martin Marietta Program. Structural panels for hot monocoque design were chosen as refractory metal honeycomb construction. Efficient structures can be built in molybdenum and columbium alloys. Typical face sheets are 0.010 inch with a core of 0.002 inch. Honeycomb panels must be sealed on all edges to prevent oxidation of the interior of the panel where adequate coating cannot be provided. Edge members must be provided to allow joining of panels to ribs either by bolting or welding.

The fabrication of the honeycomb panel cannot be considered in this program; sandwich construction is not a part of the contract effort. However, the methods of panel closure and techniques for joining one panel to another or to a rib is of interest. Current edge members and joining techniques are shown in Figure 20. The joints must be strong since all structural loads are carried by the external surfaces. Sequence of fabrication and coating for oxidation protection becomes a critical factor in determining allowable joint systems.

Radiation Shield Plus Insulated and/or Cooled Structure

Unlike hot monocoque structure, where the external structure must react all loads while operating hot, this form of construction separates the two effects. Light floating panels of refractory metals act as radiation shields, rejecting large quantities

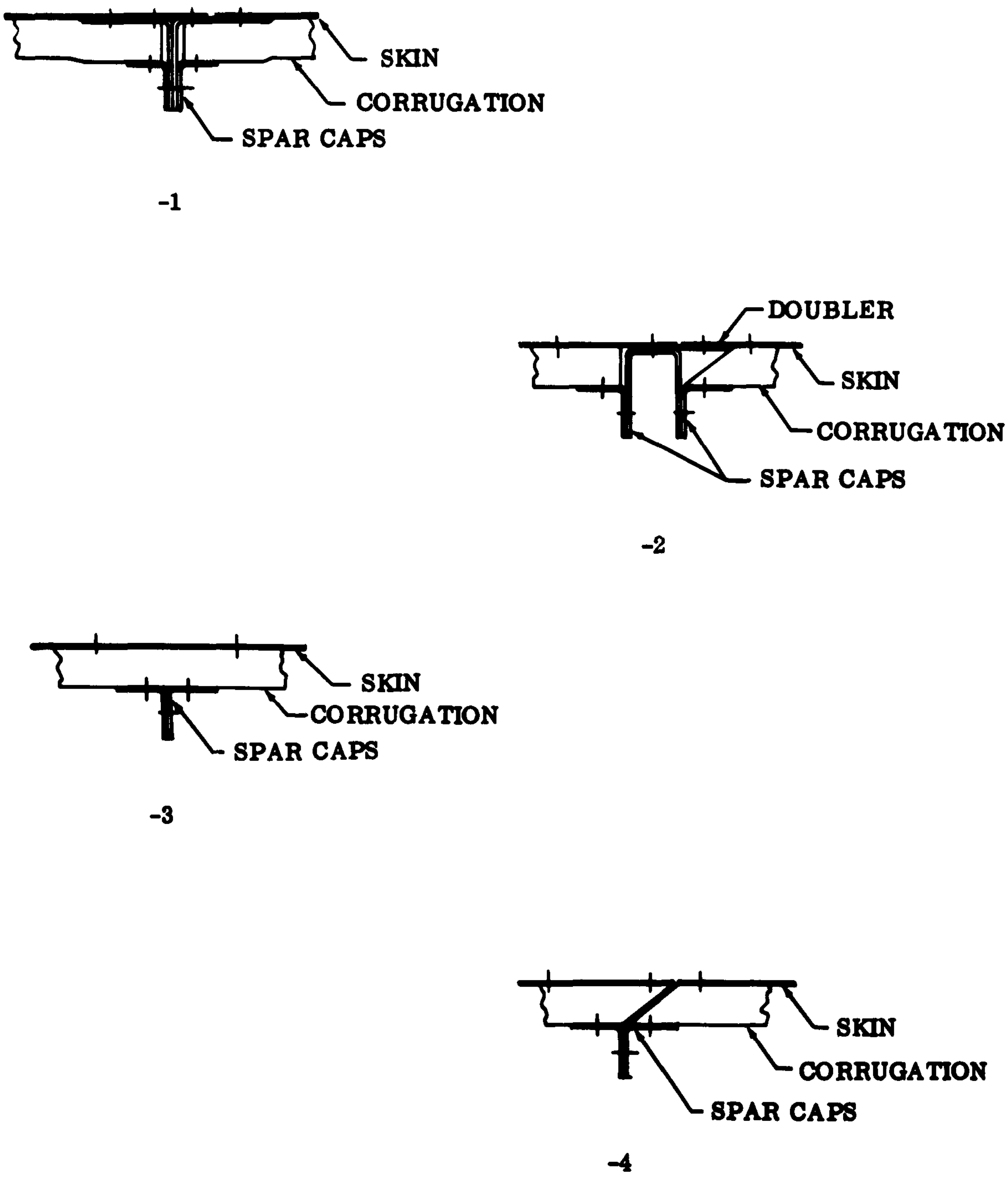


FIGURE 18. TYPICAL JOINT SYSTEMS OF PANEL-TO-SUBSTRUCTURE

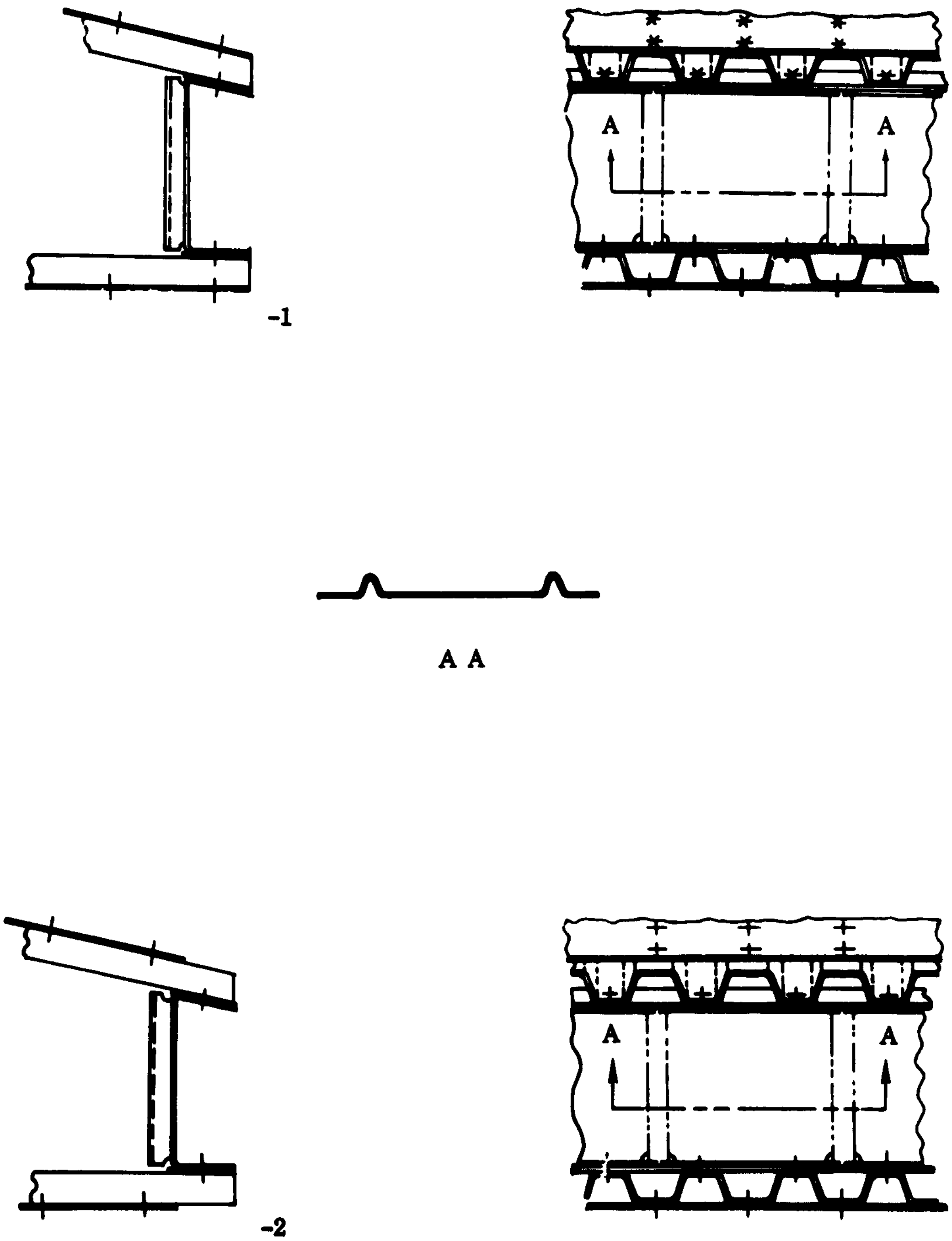


FIGURE 19. TYPICAL SPAR-PANEL STRUCTURE-HOT MONOCOQUE CONSTRUCTION

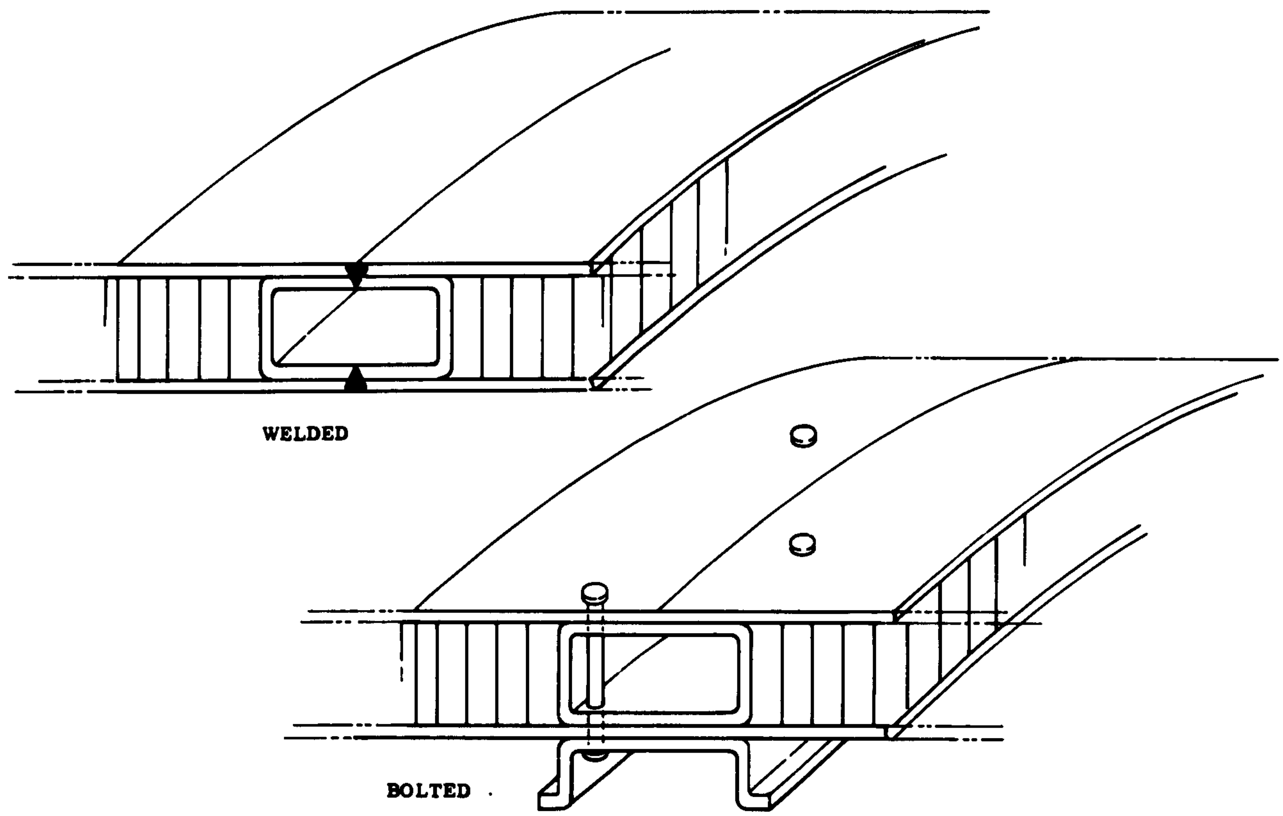


FIGURE 20. CURRENT METHODS FOR JOINING STRUCTURAL SANDWICH PANELS

of heat back to the atmosphere. Since the panels are floating, they take only air pressure loads which are light. The main load-carrying structure is located below the shields, and often separated from them by layers of insulation. Auxiliary cooling is sometimes employed to maintain low structural temperatures. In this fashion, both the hot, lightly loaded radiation shields and the cold primary structure can be designed efficiently. This type of composite structure has been shown to be extremely efficient for many typical glide re-entry vehicle configurations (Fig. 21). Examples of this type of construction investigated in the survey are:

- Manufacturing Methods for Insulated and Cooled Double Wall Structures - AF33(600)40100 Bell Aerosystems
- Manufacturing Methods and Design Procedures for Brazed Refractory Metal Honeycomb Sandwich Panels - AF33(657)7276 - Martin Marietta Corporation

Vehicle Systems Designs

- Dyna Soar
- ASSET
- Spaceplane

To operate efficiently, the heat shield panel must be able to resist air loads without excessive deflection. Support of the shield must be kept to a minimum to limit the flow of heat to the cooler substructure. Rigidity becomes of prime importance under these conditions.

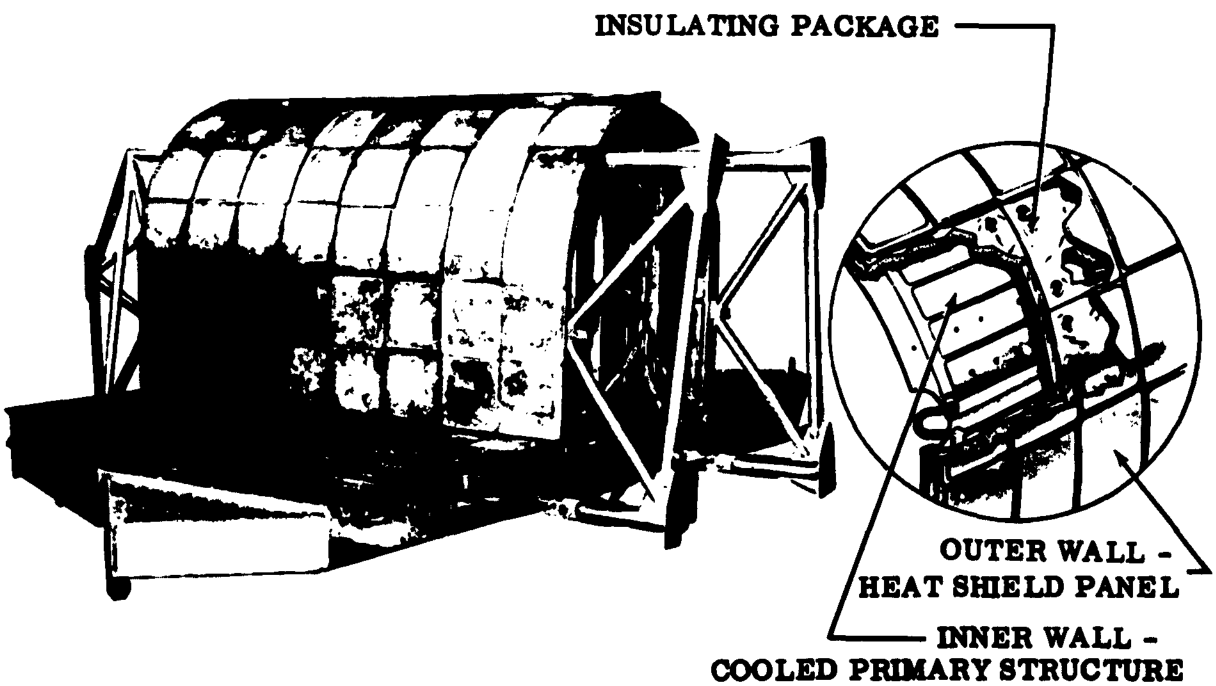


FIGURE 21. TYPICAL INSULATED AND COOLED STRUCTURE

Current heat-shield designs fall into three categories; sandwich construction, corrugation-stiffened flat sheet, and multiple channel. Examples of these types of constructions are shown in Figures 22 through 26.

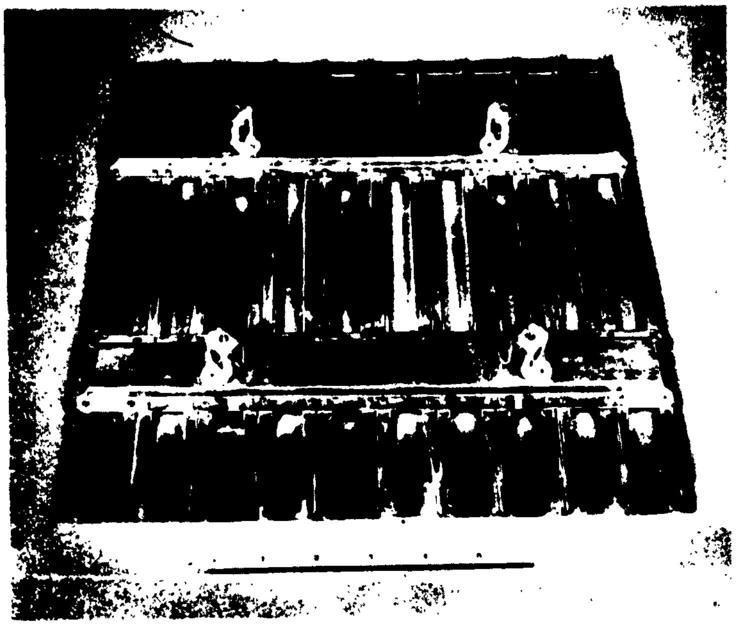


FIGURE 22. TYPICAL CHANNEL HEAT SHIELDS

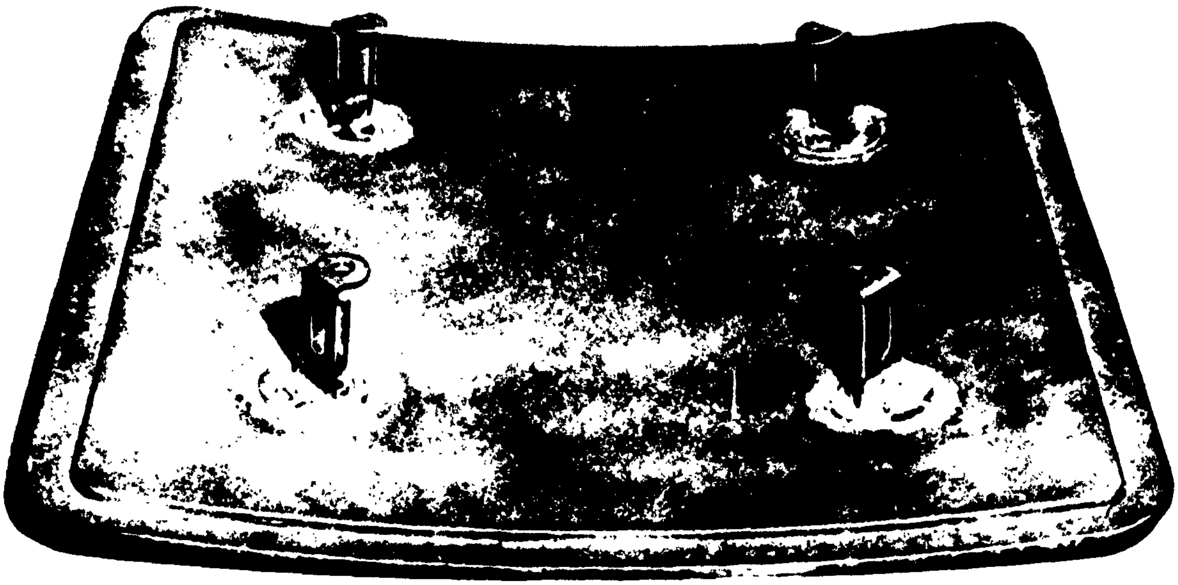
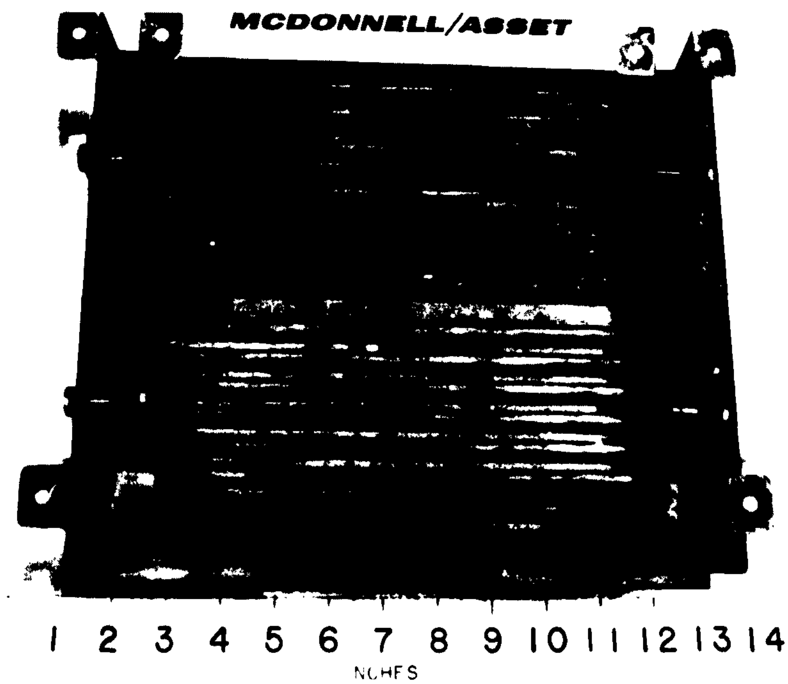


FIGURE 23. TYPICAL SANDWICH HEAT SHIELDS

A similarity exists between the various heat shield concepts. Joints of interest for application of diffusion bonding processes are:

- Edge closure of honeycomb heat shields
- Joint of corrugations to face sheets
- Joint of support clips to heat-shield panel



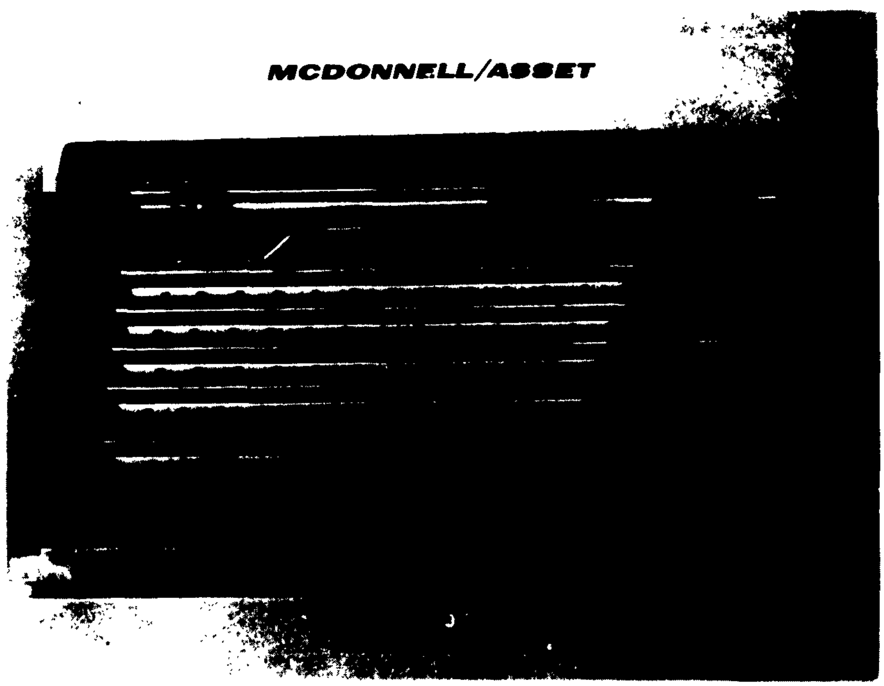


FIGURE 24. TYPICAL HEAT SHIELDS FOR PROJECT ASSET

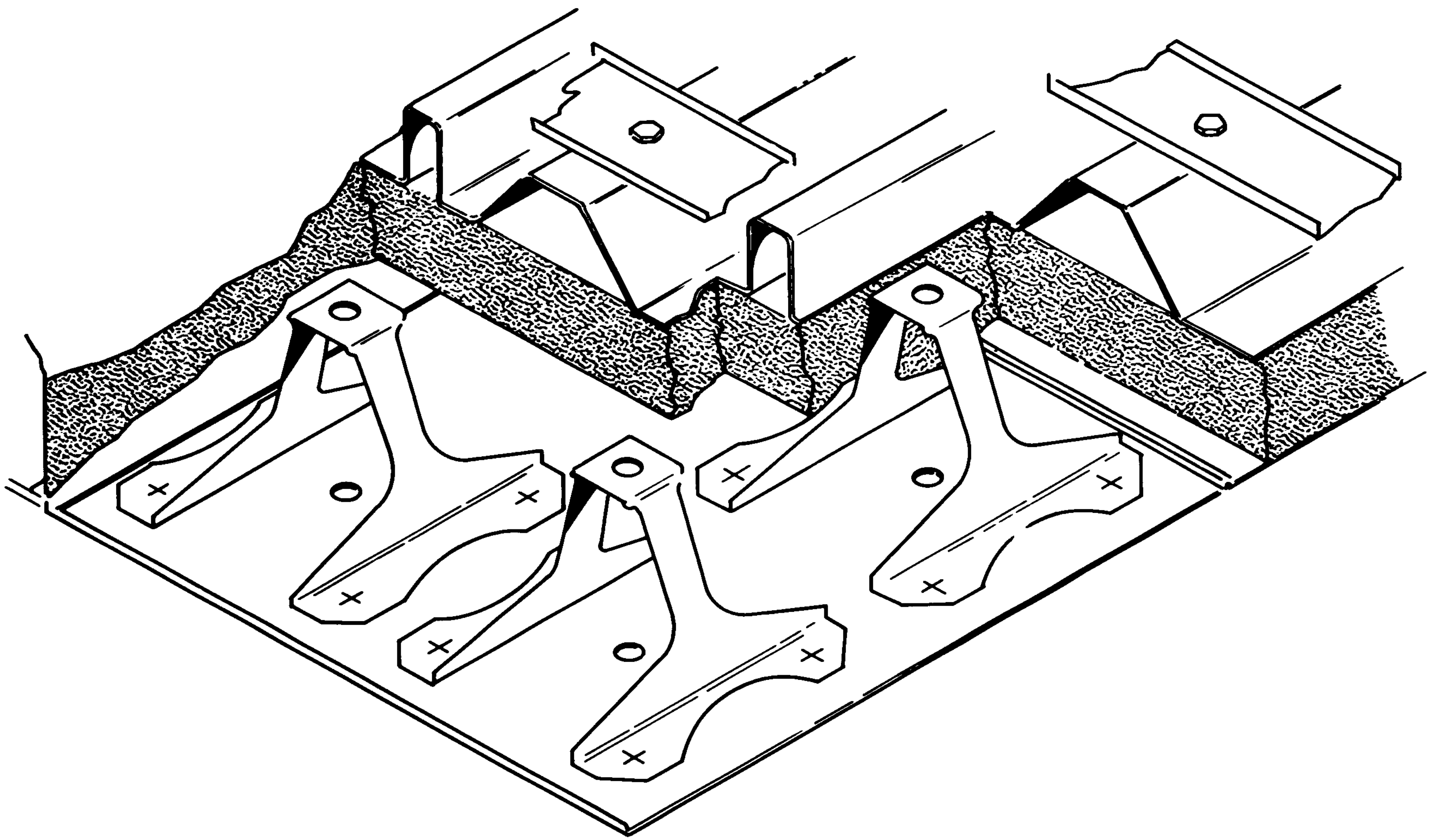


FIGURE 25. TYPICAL HEAT SHIELD PANEL FOR GLIDE RE-ENTRY VEHICLE

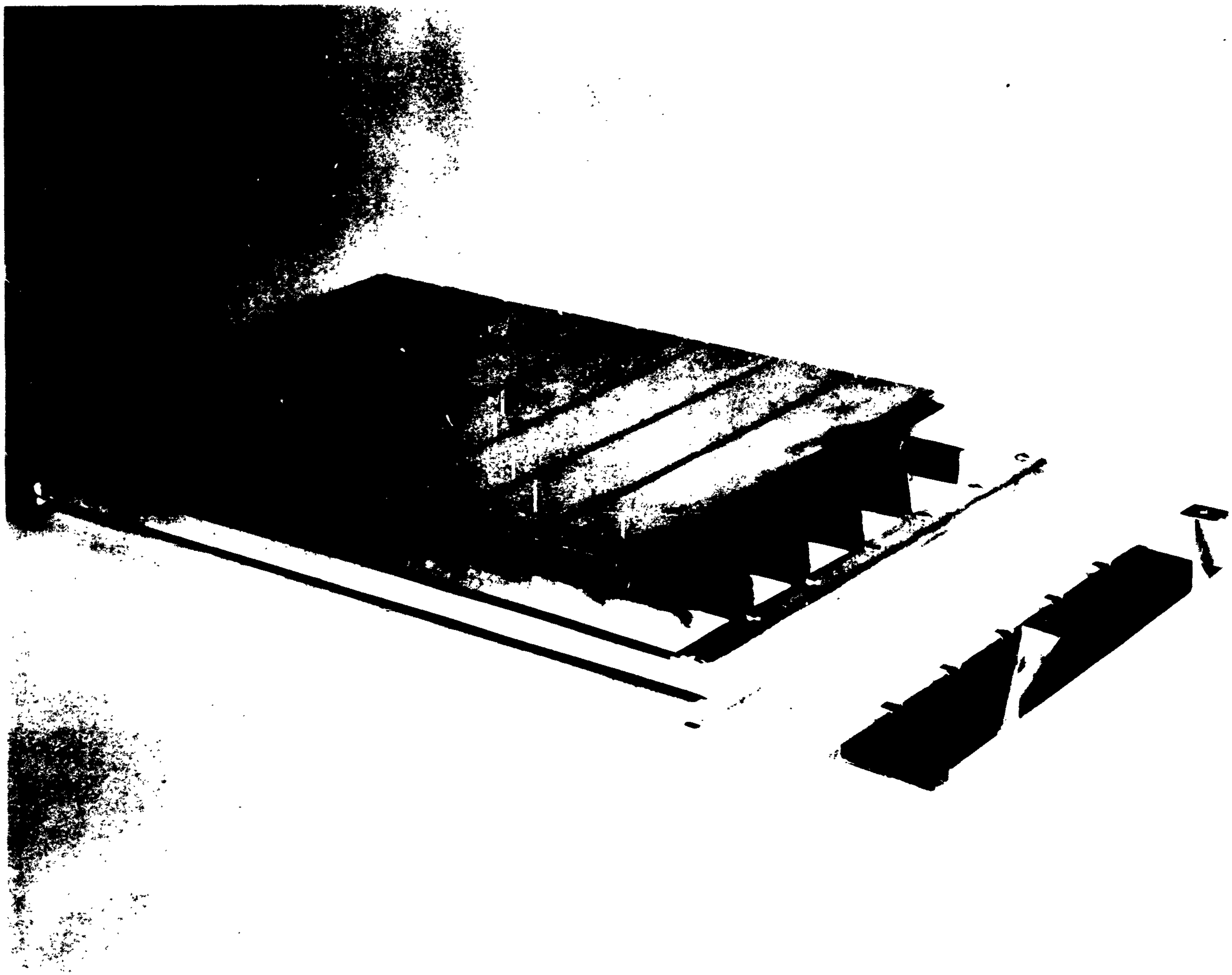


FIGURE 26. PROPOSED HEAT SHIELD FOR FUTURE GLIDE RE-ENTRY VEHICLE

3.1.2 Discussion of Joints

The survey of typical structures for future high temperature vehicle surfaces has led to selection of a series of joint systems required for fabrication of these structures. The joint systems are presented in Figure 27 for heat shields and Figure 28 for primary structure.

Heat shields of Type I are generally heavier than the others shown in Figure 27, but are currently planned for use on Dyna Soar. Using diffusion bonding, weight savings can result from smaller laps on the corrugation and elimination of rivets (current method of joining). Reliability becomes higher because of the simplicity of coating the diffusion bonded assembly.

The Type II shield can be made more efficiently with diffusion bonded joints because of the higher panel strength obtainable with continuous seam joints between sheet and corrugation. Coating sequences are simplified by this procedure.

The Type III shield is currently made with bolted connections between channels and brace. The diffusion bonded joint again eliminates weight of bolts and simplifies coating processes.

The Type IV shield cannot be made any lighter through the use of diffusion bonding. Currently, panel edges and tabs are brazed while the honeycomb panel is being brazed. Should this process prove to be unsatisfactory, the clips and edges can be joined by diffusion bonding.

Structural joints are those capable of joining brazed refractory metal honeycomb sandwich panels. The joints must be continuous, and able to withstand high normal and planar shear loads. Their design is particularly significant because the theoretical efficiency of brazed sandwich construction for hot structure depends largely on the ability to join these panels with light strong joints. Current methods of joining panels are welding and bolting. Welding may damage the wrought material properties and introduce distortions. Bolting can be quite heavy. The main advantage of diffusion bonding for these structures is the ability to fabricate stiffeners tailored to joining panels. Such stiffeners cannot be made currently by any technique other than welding. The ability to build up a joint of properly placed members allows a latitude in design optimization not now available in a honeycomb structure.

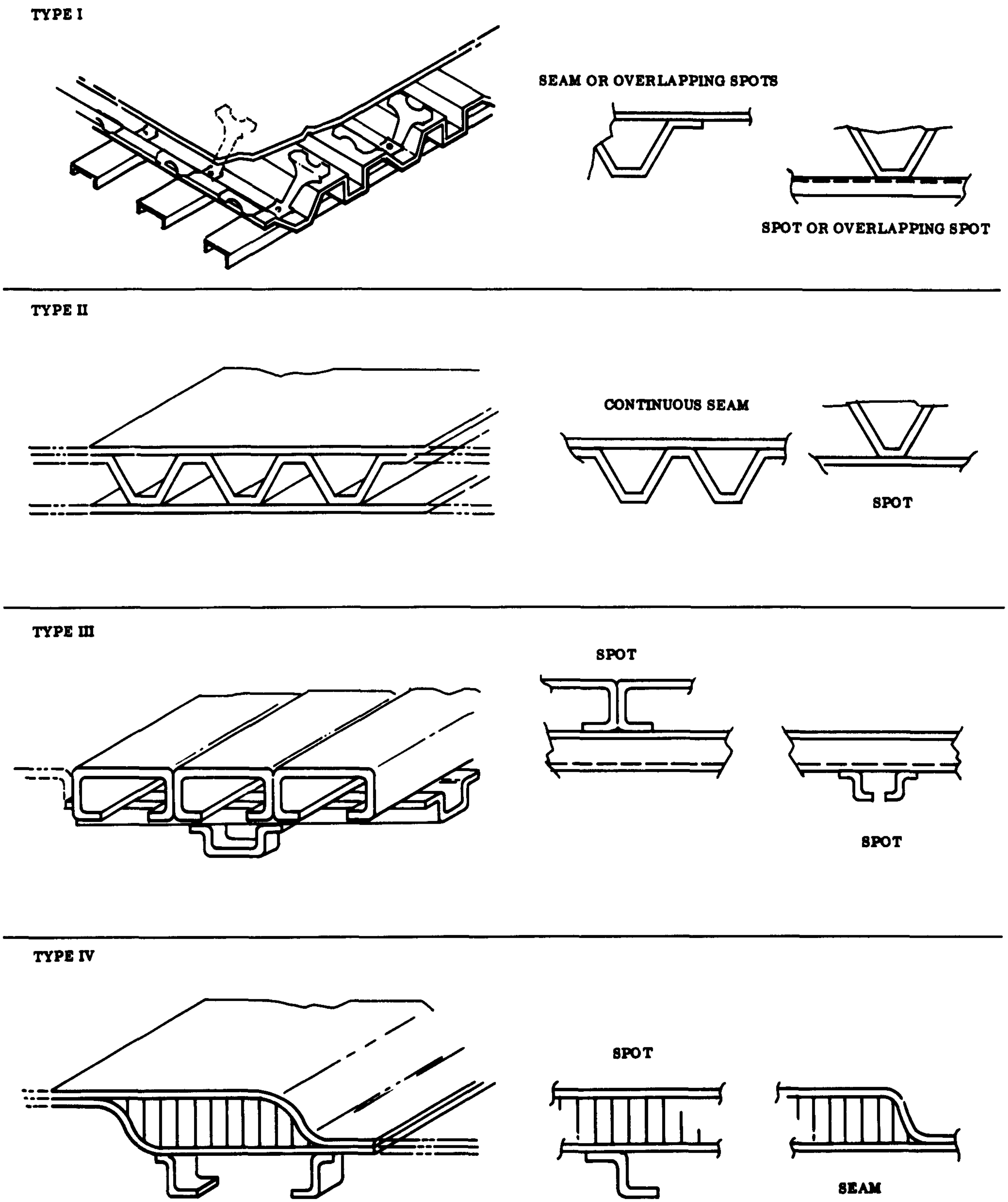


FIGURE 27. TYPICAL JOINTS FOR HEAT SHIELDS

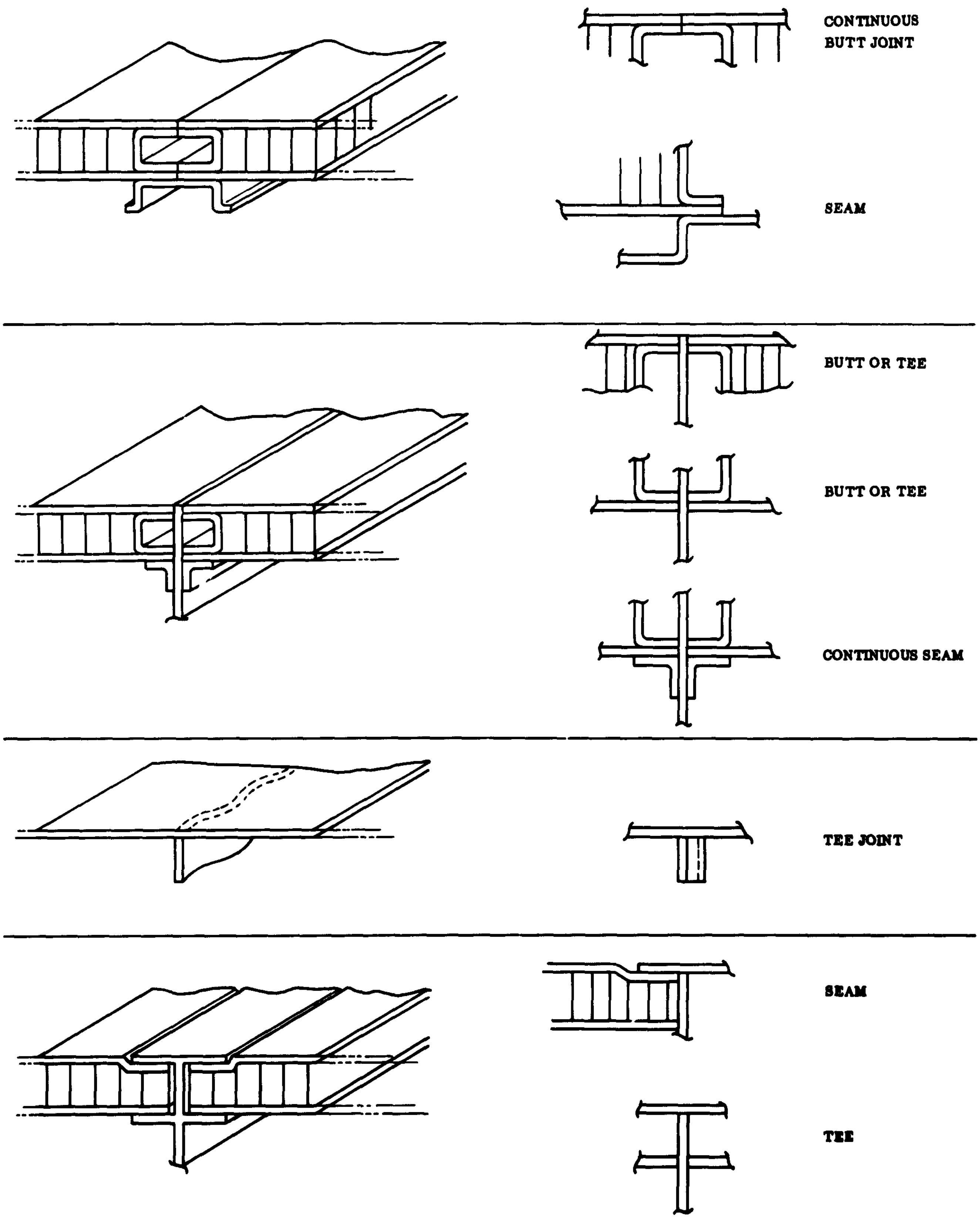


FIGURE 28. TYPICAL JOINTS FOR STRUCTURAL PANELS

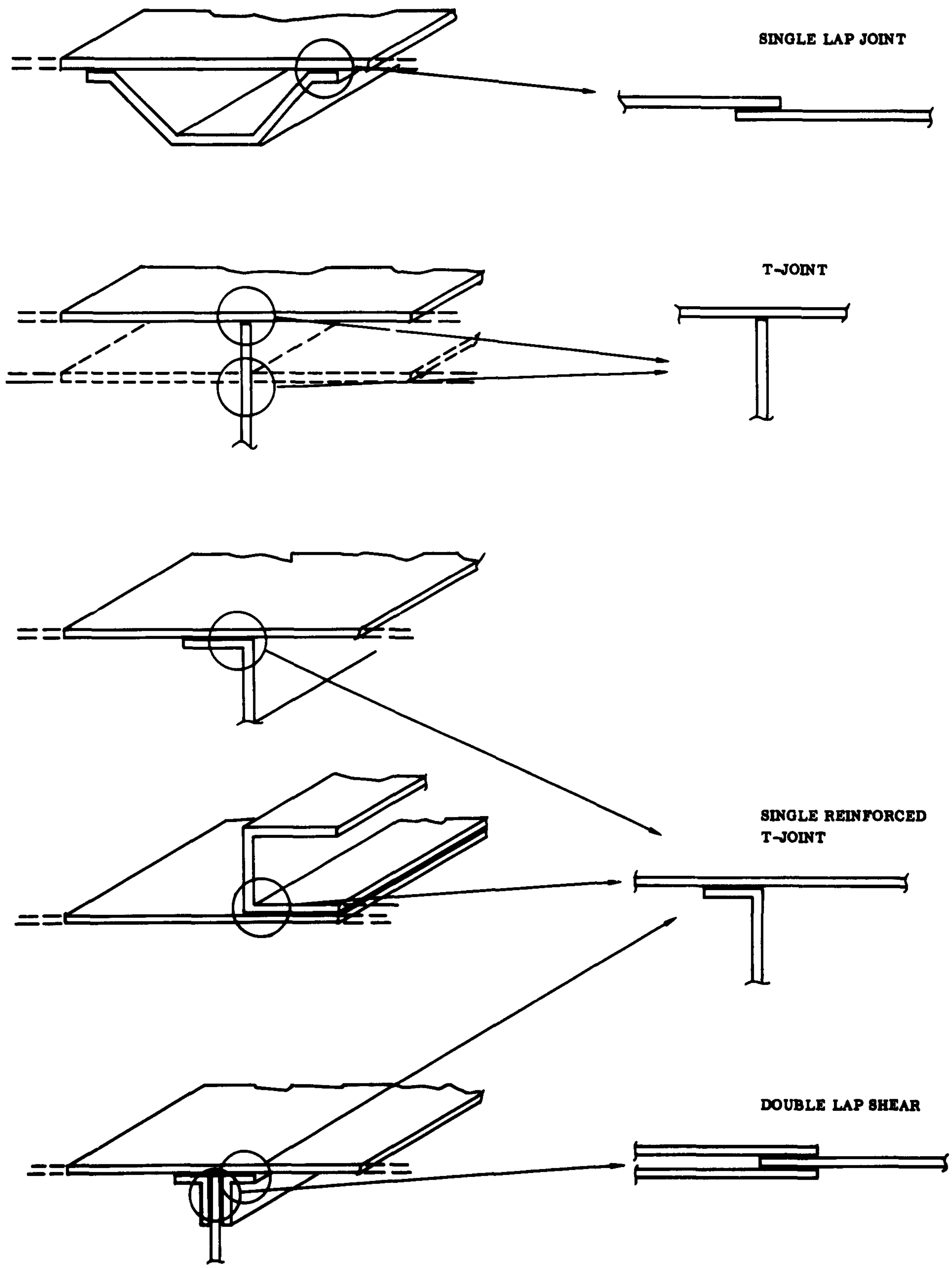


FIGURE 29. STRUCTURAL ELEMENTS AND STUDY JOINTS

Choice of Typical Joint Systems

Based on the above discussions, a series of typical joints is recommended for initial study on this program. These joints are shown in Figure 29, and represent the majority of joint problems to be met in future structures.

Diffusion bonding has recently advanced to the point where it can be considered seriously for use in flight structures. Therefore, the structural systems designed to date have not attempted to take full advantages of that joining process. As work progresses on this program, many new ideas for efficient joining systems will be generated, leading to effective structural joints. The joints shown in Figure 29 will help find those systems.

3.2 DEVELOPMENT OF TOOLING

3.2.1 Induction Spot Bonder

To accomplish solid state bonding of refractory metals, it is necessary to bring the clean surfaces together with very intimate contact; heat to a sufficiently high temperature to produce good atomic mobility; hold for sufficient time to allow diffusion to occur; and maintain a protective atmosphere to prevent oxidation and embrittlement of the joint materials.

A device was developed at Solar during an earlier investigation that produced excellent joints on small lap specimens. This bonder is shown in operation in Figures 30 and 31. The bonding force is applied hydraulically through high density aluminum oxide anvils. A protective atmosphere is maintained within a quartz tube, enclosing the anvils and specimen, by purging with high purity inert gas or dry hydrogen. The specimen is heated by conduction from an inductively heated tungsten disc.

This device serves as a research tool and permits close control of temperature, pressure, and atmosphere. Another desirable feature is the small specimen size and the related economy when the joining parameters of the expensive refractory metals are being investigated.

3.2.2 Resistance Spot Bonder

The development of equipment for the bonding of structures on a semi-production basis is awaiting answers to questions such as the following:

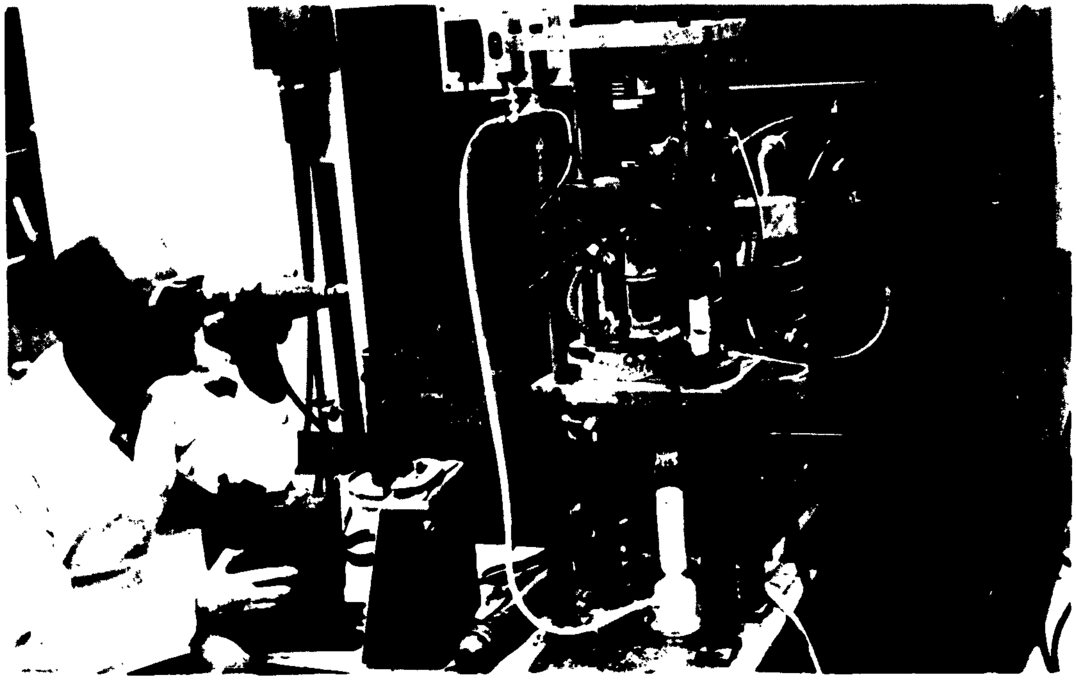


FIGURE 30. GENERAL VIEW OF INDUCTION BONDER

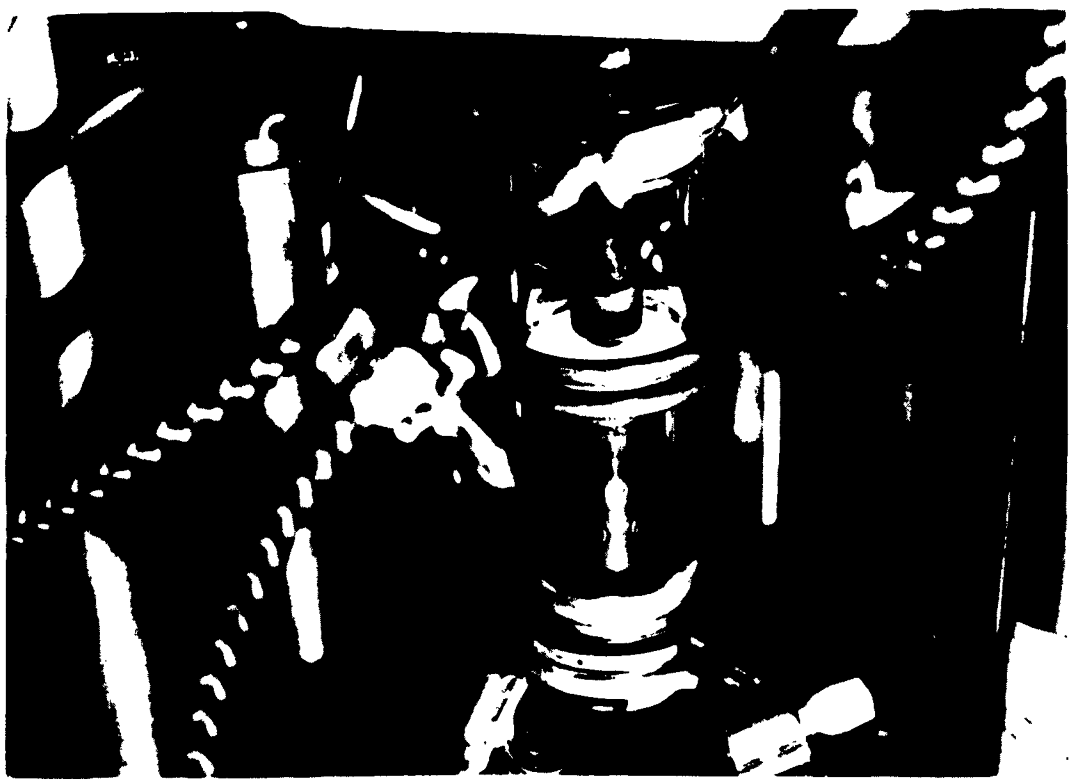


FIGURE 31. CLOSE-UP OF INDUCTION BONDER

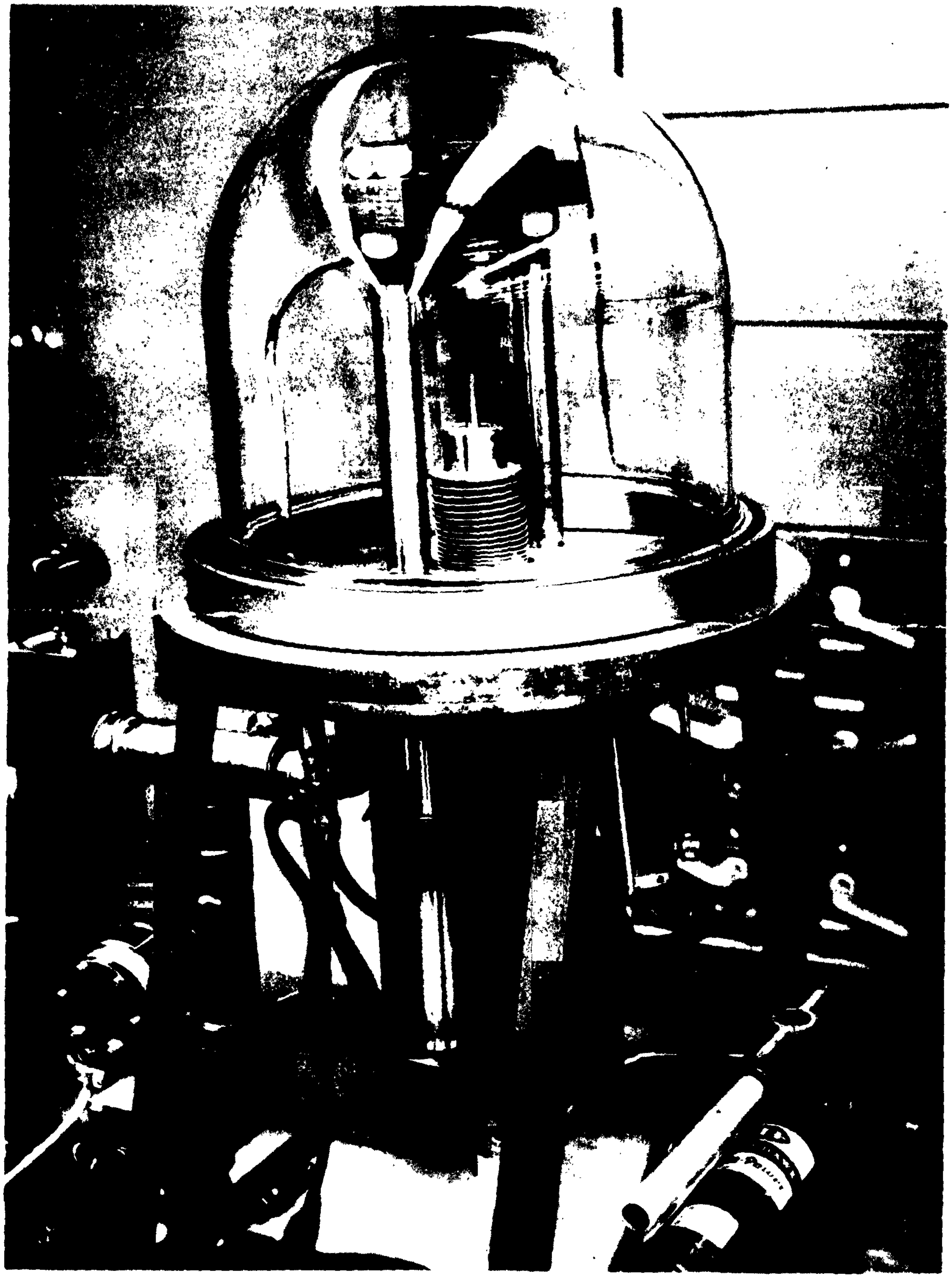


FIGURE 32. RESISTANCE BONDER

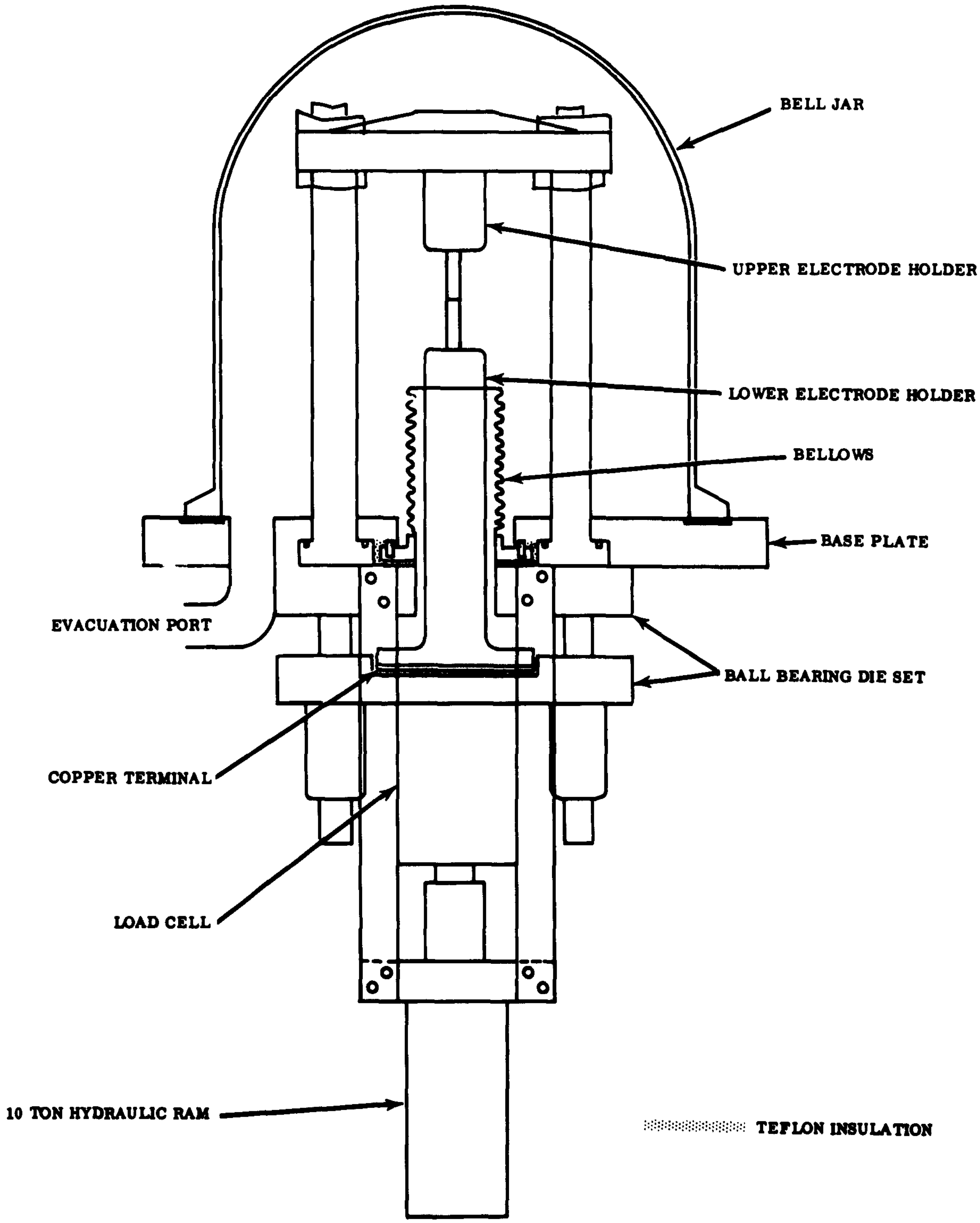


FIGURE 33. SCHEMATIC DRAWING OF RESISTANCE BONDER

1) What method of heating will be used?

2) What materials are best suited for anvil and electrode construction?

3) What is the maximum tolerable impurity in the protective atmosphere?

Induction heating is being used with good results with the laboratory bonder described above. Induction heating is also being considered for the prototype bonder, but the heating of irregularly shaped sheet metal structures with close temperature control appears impractical.

Heating by passing large, controlled quantities of electrical current through the joint area, as in spot and seam welding, is also being investigated and appears quite promising. The main problem with resistance heating is the choice or development of electrode materials. They must be electrical conductors, possess good compressive strength at high temperatures, and resist sticking to the material being joined.

The resistance heated spot bonder, shown in Figure 32, is currently being used to determine the practicability of this method of heating. Figure 33 is a schematic drawing showing the essentials of construction and operation. The upper electrode holder is rigidly mounted to the vertical columns and the lower electrode holder moves vertically, guided by a precision ball bearing die set and sealed at the base plate with a flexible metal bellows. The lower electrode is raised by the extension of a hydraulic ram. The squeeze force is measured by a load cell located between the ram and the lower electrode holder.

A glass bell jar is placed over the electrodes and sealed with a gasket against the base plate. The air is removed from the chamber with a high vacuum system. A vacuum of 5×10^{-5} Torr has been attained in the chamber. Bonding can be done in high vacuum or at higher pressures by backfilling with a gas.

Three TZM double lap specimens (.05 in. x .40 in.) have been bonded using 1.5 mil tantalum foil as a bonding aid. Bonding was accomplished by passing 1600 amperes for 60 seconds while squeezed with a force of 1000 pounds. This is equivalent to 80,000 amp/sq in. and 50,000 psi. W-2Th electrodes (3/8 in. dia) attained

an optical temperature of 1900 F during bonding and the chamber pressure increased from 5 x 10^{-5} to 5 x 10^{-4} Torr. When tested in tension at room temperature, the specimens failed at 305, 345, and 295 pounds of load.

With this bonder a systematic study is planned to determine the following:

- Current-pressure-time parameters as a function of bond strength
- The selection of optimum material for electrode construction
- The effect of impurity level of protective atmosphere on bond strength and embrittlement

3.3 SELECTION AND PROPERTIES OF ALLOYS

3.3.1 Background

This program was set up to examine diffusion bonding processes for six refractory metal foils in two gages. The alloys were tentatively defined by ASD as two columbium, two molybdenum, one tantalum, and one tungsten. The gages were to be 0.006 to 0.008 inch and 0.010 to 0.012 inch. For three reasons, it became desirable to make certain changes in the alloy selection. These reasons were:

1. Unavailability of more advanced alloys for the initial exploratory work.
2. Chemical similarity of current molybdenum alloys suggested that joining and coating problems would be similar on all alloys.
3. Chemical dissimilarity of current columbium alloys and claimed effects of chemistry (such as detrimental effect of zirconium on some coatings) suggested additional columbium alloys should be studied.

In line with these reasons, the following alloys were chosen.

Preliminary work. Choice was made on grounds of availability, background information on coating and general wide experience.

Molybdenum: TZM alloy (MO-0.5Ti-0.1Zr)

Columbium: D36 alloy (Cb-10Ti-5Zr)

Tantalum:	90Ta-10W alloy
Tungsten:	Pure

<u>Advanced work</u> (tentative selection).

Molybdenum:	TZM alloy (Mo-0.5Ti-0.1Zr)
Columbium:	D36 alloy (Cb-10Ti-3Zr)
	B33 alloy (Cb-4V)
	No selection at present time
Tantalum:	T111 alloy (Ta-8W-2Hf)
Tungsten:	No selection at present time

The 90Ta-10W alloy and pure tungsten were chosen for availability to get the program started. The stronger T111 alloy is proposed for substitution in subsequent work. The molybdenum alloy TZM was available at the start of the program and will be carried throughout the work. It is proposed to substitute a third columbium alloy instead of the second molybdenum alloy to keep the total number at six.

3.3.2 Columbium Alloys

The selection of two moderate strength columbium alloys was based on the marked differences in chemistry. The moderate strength columbium alloys contain Zr (D14), Ti (D36), and V (B33). Choice of a moderate strength alloy was based on the desire to include the three principal alloying elements (Ti, Zr, and V) and led to D36 (Cb-10Ti-5Zr) and B33 (Cb-4V). Higher strength columbium alloys generally contain Mo (B66), W (Cb752 and X110), Ta (FS85), or a combination of these metals. No selection has been made of a higher strength columbium alloy, but this decision will be made soon in conjunction with ASD. Factors that will influence this choice have been examined, and are believed to be:

- Large percentages of tantalum are required to strengthen columbium (FS85 has the composition Cb-28Ta-12W-1Zr), and these increase the density sharply (FS85 has a density of 0.391 lb/cu.in. against 0.305 lb/cu. in. for B66 alloy

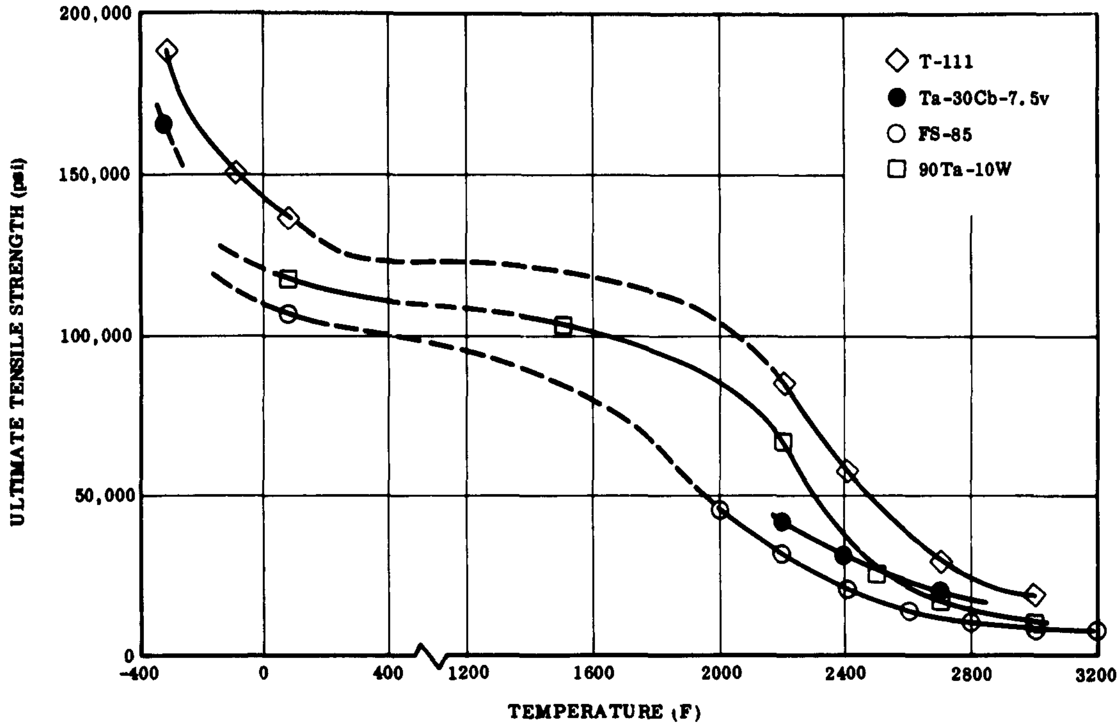


FIGURE 34. ULTIMATE TENSILE STRENGTH OF TANTALUM ALLOY AND FS85

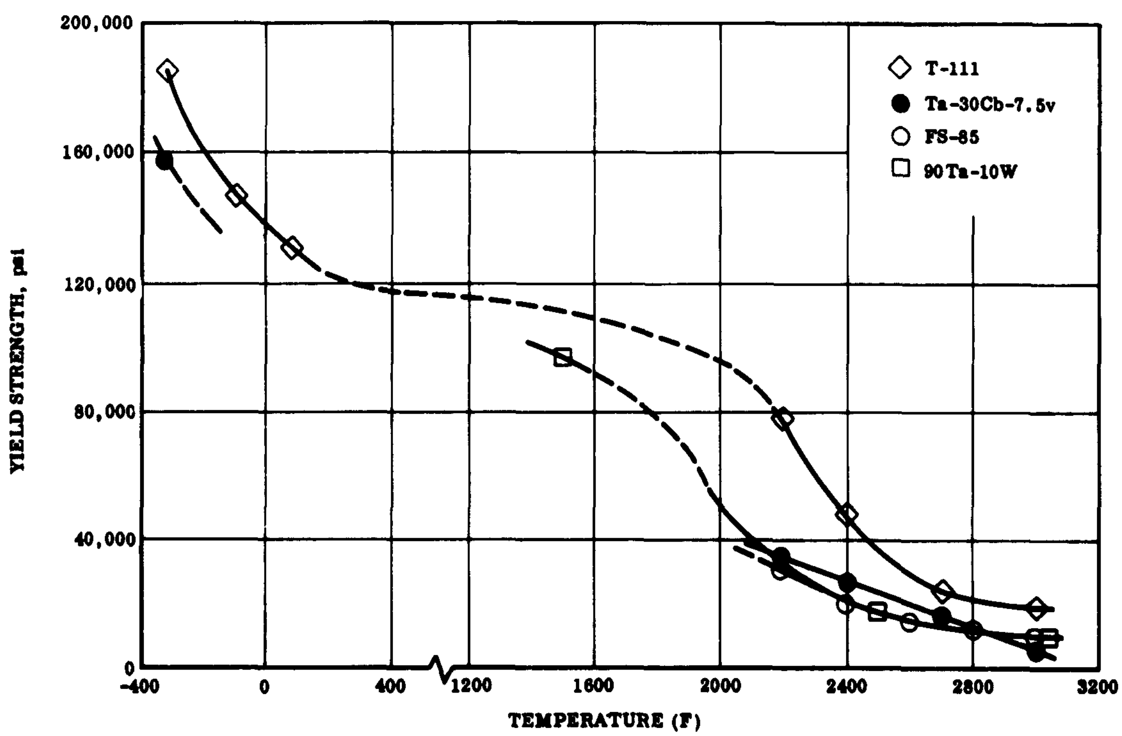


FIGURE 35. YIELD STRENGTH OF TANTALUM ALLOYS AND FS85

(Cb-5V-5Mo-1Zr). The advantages of high tantalum content alloys include a higher melting point with strength loss above 2500 F not as rapid as for tantalum-free alloys, and higher elastic modulus.

- The adverse effect of large additions of Group VI elements on interstitial reactions in heat treatments, is illustrated by the irreversible embrittlement of F48 (Cb-15W-5Mo-1Zr) on welding and has tended to restrict additions of these elements. Recently developed alloys (B66, Cb752 and X110) have limited additions of these elements to make the alloys weldable. Diffusion bonding will circumvent this embrittlement problem so that higher strength alloys such as F48 or F50 might be reconsidered if available in foil form.

3.3.3 Tantalum Alloys

The selection at the beginning of the program of 90Ta-10W on the grounds of availability has already been discussed. The selection of the advanced alloy was deferred until more data was available. Recent developments have made Westinghouse's T111 commercially available on a limited basis, and the selection has been made from four alloys available at the present time. These are: T111, 90Ta-10W, FS85, and Ta-30Cb-7.5V. Although FS85 is basically a columbium alloy, the mechanical properties are comparable, especially on a strength-to-weight basis. The mechanical properties of these four alloys were used as the principal basis for selection.

The tensile strength, yield strength, and strength/density values are shown in Figures 34, 35 and 36. Other miscellaneous data is listed in Table VII. The strength properties of T111 substantially exceed those of the other alloys in all instances except that of strength/density at very low temperatures. However, T111 still exceeds the properties of 90Ta-10W at low temperatures, and it has excellent ductility, 18 percent at -320 F. The recrystallization temperature of T111, (2500 F) is acceptable. The excellent weldability of Ta-30Cb-7.5V (probably related to its high solubility for interstitials) is not a factor in the choice of an alloy for diffusion bonding. Hence, T111 alloy has been proposed as the advanced tantalum alloy for this program. Delivery of 0.012 inch sheet in eight to ten weeks has been promised.

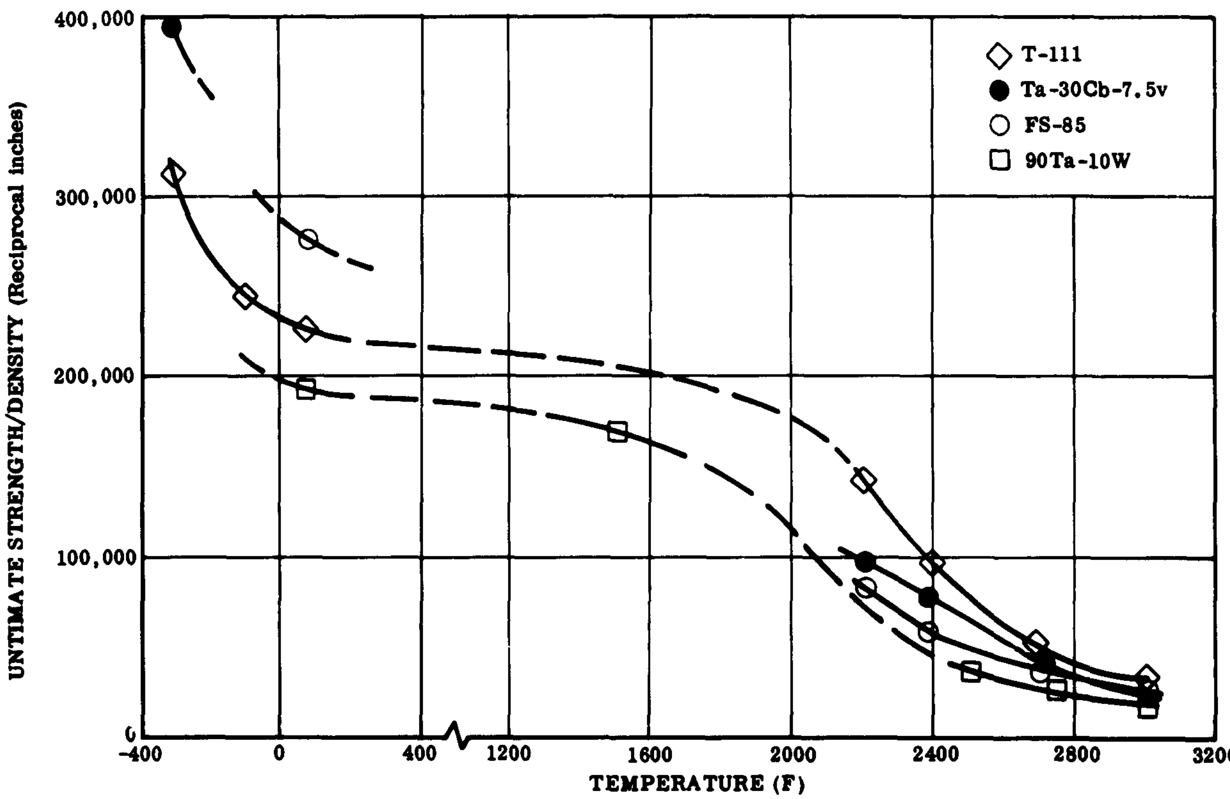


FIGURE 36. STRENGTH/DENSITY OF TANTALUM ALLOYS

TABLE VII

PHYSICAL DATA FOR TANTALUM-BASE AND FS85 ALLOYS

Designation	Composition	Density (lb/cu in.)	Recrystallization Temperature, (F)	Elongation at -320 F (%)
T-111	Ta-8W-2Hf	0.604	2500	18
FS-85	Cb-27Ta-12W-0.5Zr	0.39	2400	--
--	Ta-30Cb-7.5V	0.426	2200	--
90-10	Ta-10W	0.607	2300	--

3.4 BONDING STUDIES

Preliminary work was started to study the effect of surface finish and intermediate foil thickness. Surface finish should be studied because the refractory alloy sheets presently available vary from a smooth mirror finish to a relatively rough finish characteristic of either pack rolling or extensive acid etching. The final results of this study might determine whether a standard surface finish is desirable for more consistent diffusion bonding. It would also determine whether the local surface cold working produced by abrading would improve the bonding process.

The second study was conducted to investigate the effect of intermediate foil thickness on the strength of the resulting bond. Both studies are incomplete, and more work will be done later in the program.

3.4.1 Surface Finish

The effect of surface finish was investigated with bonds made from TZM and intermediate titanium foil. To ensure a uniform surface condition, the TZM specimens were lapped on a Crane Lapmaster 12 until all the specimens had a uniformly smooth, flat surface. Approximately 0.75 mil per side was removed from the 1/2 by 3/4 inch specimens before a uniform thickness and surface finish was attained. The specimens were then processed with the cleaning and etching solutions normally used in the program. A surface finish of three microinches was obtained on the TZM surfaces.

Bonds were made from TZM specimens having surface roughness of three, twelve, and thirty-five microinches rms. The first was the as-lapped surface; the other two were prepared by hand abrading the lapped specimens with 320A and 100M abrasive papers. All of the bonds were made under the same conditions, with the results of the study being shown in Table VIII.

TABLE VIII

INVESTIGATION OF SURFACE ROUGHNESS

Surface Roughness	Number of Specimens	Breaking Load, (lb)
3	3	387
12	3	373
35	3	313
As received - 35	3	330
As received - 35 (Table V)	4	300

Parent material:	0.012 in. TZM
Interfacial material:	0.3 mil titanium foil (one thickness)
Joint type:	Double lap
Joint area:	2 - 0.050 in. x 0.45 in.
Heating time:	390 sec
Pressure:	3000 psi
Pressure dwell:	60 sec (330 to 390 sec)
Temperature:	1725 F
Atmosphere:	Gettered A

On the basis of this study, the best results were obtained with the very smooth surfaces. The results of these tests showed a 20 percent increase in bonding strength over that of specimens made with as-received material. The surface cold work produced during abrasion did not have any apparent effect on the results. The best surface condition for diffusion bonding is a smooth finish.

3.4.2 Intermediate Foil Thickness

One and three thicknesses of 0.3 mil titanium foil were used in joining 0.012 inch TZM for this study. A bonding pressure of 12,000 psi was used, with the other bonding conditions being identical to those in Table VIII. With one layer of titanium, four specimens averaged 473 pounds breaking strength. With three layers of titanium, three specimens broke at an average of 388 pounds.

These results are preliminary, but indicate that a thickness effect exists and that more work will be necessary to determine the optimum thickness. Because of the larger difference in strength between TZM and Ti at elevated temperatures, it is anticipated that thickness effects will become more pronounced at higher temperatures.

3.5 COATINGS FOR JOINTS

Potential Air Force applications, for diffusion bonded refractory metal structures, are primarily in the hot parts of aerospace vehicles exposed to an oxidizing environment. Since refractory metals are not oxidation resistant above 800 F, protective coatings must be an integral part of any hot structure. Because of the intimate relationship between coating reliability and joint design, consideration must be given to coating requirements at the outset of this program.

Coating processes for refractory metals are of two basic types, the first is pack cementation, and the second is alloying with a molten metal. In the present stage of development, the latter is not sufficiently advanced to warrant immediate consideration for high reliability coatings. A few of the available processes are summarized in Table IX. It is not proposed to discuss the relative merits of each process because this has been the subject of many evaluation programs including one at Solar (Contract AF33(657)-9443) on foils of 0.002 to 0.010 inch. More important at this stage is an analysis of the basic processes to determine effects that will influence the protection of joints.

TABLE IX

TYPES OF COATING PROCESSES FOR REFRACTORY METAL

Vendor	Mo	Cb	W	Ta
Chromizing	Complex Silicide Cementation	Complex Silicide Cementation	Simple or Complex Silicide Cementation	--
Chromalloy	Complex Silicide Cementation	Complex Silicide Cementation	Simple or Complex Silicide Cementation	--
Pfaudler	Complex Silicide Cementation	Complex Silicide Cementation	Simple or Complex Silicide Cementation	Complex Silicide
Vought	Complex Silicide Cementation	Complex Silicide Cementation	Simple or Complex Silicide Cementation	--
Batelle	--	--	--	Complex Silicide
American Machine and Foundry	Complex Silicide Cementation	Complex Silicide Cementation	Simple or Complex Silicide Cementation	--
TAPCO (TRW)	--	Complex Silicide Cementation	--	--
General Technology Corporation	Complex Silicide Cementation	Complex Silicide Cementation	--	--
General Electric Co. (or McDonnell)	Al Alloy Slurry	Al Alloy Slurry	--	--
General Telephone & Electronics	Al Alloy Slurry	Al Alloy Slurry	Complex Silicide	Al-Sn Slurry

In the typical pack cementation process, the part is submerged in a pack containing the metals to be deposited, an activator such as a halide salt, and an inert powder such as alumina to prevent sintering. The pack is heated to a temperature between 1800 and 2300 F for several hours. Pressures may be atmospheric or below. At the coating temperature, a series of reactions occur which result in a net transfer of the metallic pack material to the part. The following series of equations may be regarded as typical of the cycle:

1. $2KF + Si \longrightarrow SiF_2 + 2K$

2. $2SiF_2 + \text{Part} \longrightarrow SiF_4 + Si \text{ (part)}$

3. $SiF_4 + Si \text{ (pack)} \longrightarrow 2SiF_2$

The activity of the silicon on the part is reduced below that of the silicon in the pack by the formation of silicides. The net effect is a transfer of silicon to the part. A general appreciation of the reactions involved is important in a study of the problems of coating joints.

Figure 37 shows typical configurations of joints. Figures 37A, B, and C show a single lap joint with intermediate metal foil (shown much thicker than actually will be used). The general problem of compatibility of the silicide formed on this foil with that formed on the refractory metal must be solved first. Thus, titanium foil forms excellent bonds with molybdenum, but the Ti-8.5Si eutectic is at 2425 F, whereas the corresponding eutectic with zirconium is at 2490 F. Coverage by the foil is important. The incomplete lap shown in 37A requires the coating to have sufficient throwing power to coat the re-entrant surfaces. The foil shown in 37C may present no problem because the silicon will convert the free ends entirely to silicide if the thickness of the intermediate foil is less than twice the typical coating thickness. The brittle tag ends of the foil will break away in cleaning the part after removal from the pack, leaving a situation similar to the ideal represented by 37B. Figures 37D and E represent two types of reinforced T-joint. Bonding Type E at the bottom of the sheet creates a hole the length of the joint, which cannot be adequately coated. Hence, joint D is preferred.

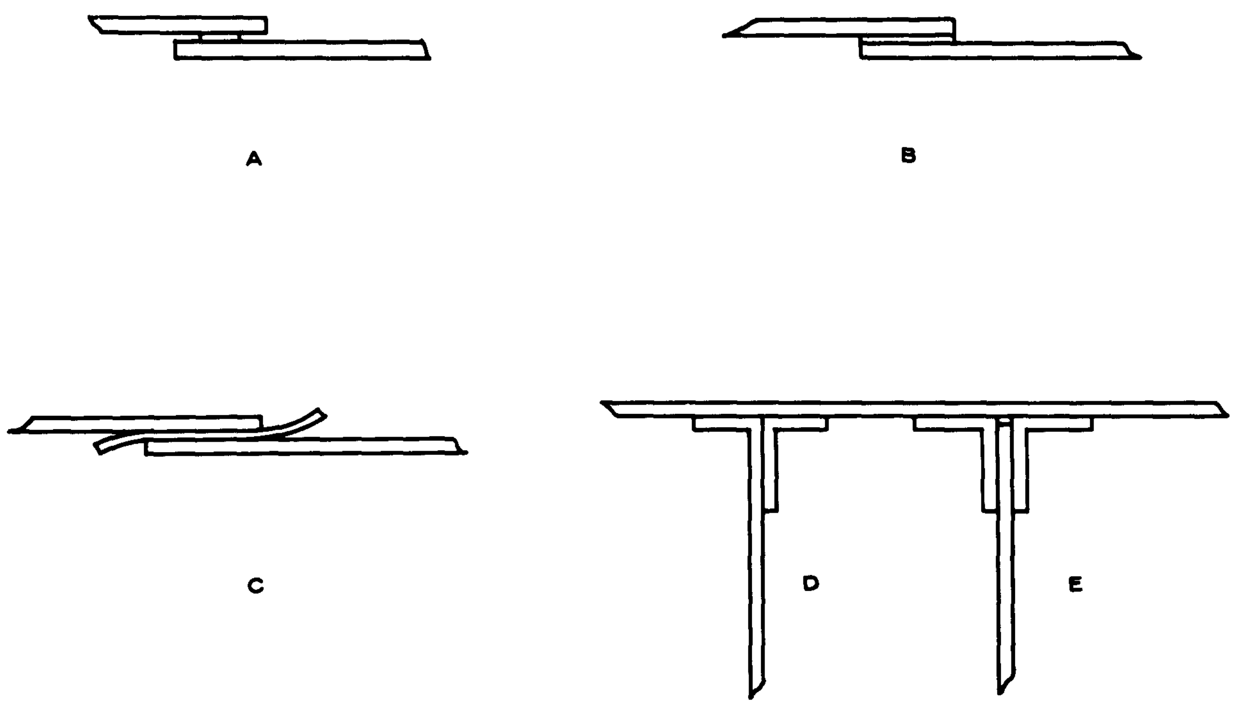


FIGURE 37. COATING PROBLEMS WITH JOINTS

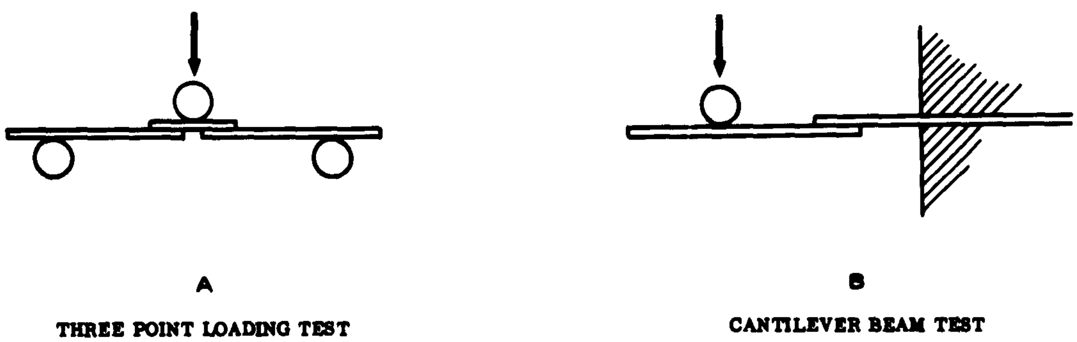


FIGURE 38. TEST SPECIMEN DESIGNS TO DETERMINE PEEL STRENGTH

These preliminary considerations in the coating-joint design will be extended as joints become available for coating.

3.6 TESTING OF JOINTS

The problem of poor "peel" strength of lap joints was discussed in Section 2.3. Analysis of typical applications of lap joints, e.g., attachment of clips to heat shields, shows that stresses other than pure shear will be encountered, and higher strength in a direction normal to the lap is essential. This analysis requires a non-standard test, and several simple test specimen designs have been considered. Figure 38 shows two designs that are under consideration to determine peel strength of joints. Preliminary tests will be made of both designs to determine their relative merits.

IV. SCHEDULE AND FUTURE WORK

4.1 SCHEDULE

Figure 39 compares the schedules proposed and schedules that are being achieved in this program. The breadth of the concepts to be evaluated in Phase I was not known until the literature survey was complete with the result that completion of this work was delayed by unexpected requirements of materials. Phase II has been in progress for over a month. In general, work is on schedule.

4.2 FUTURE WORK

Work in the next quarter will include the following:

1) Study loading systems on selected joints to lead to recommended test procedures

2) Develop design data for prototype bonder using newly constructed resistance spot bonder

3) Begin construction of prototype bonder

4) Develop general information on diffusion bonding process, e.g., surface finish and intermediate foil thickness effects

5) Select high strength columbium and tungsten alloys in conjunction with ASD

6) Develop specific bonding processes for each of the six refractory metals

7) Submit preliminary joints for coating

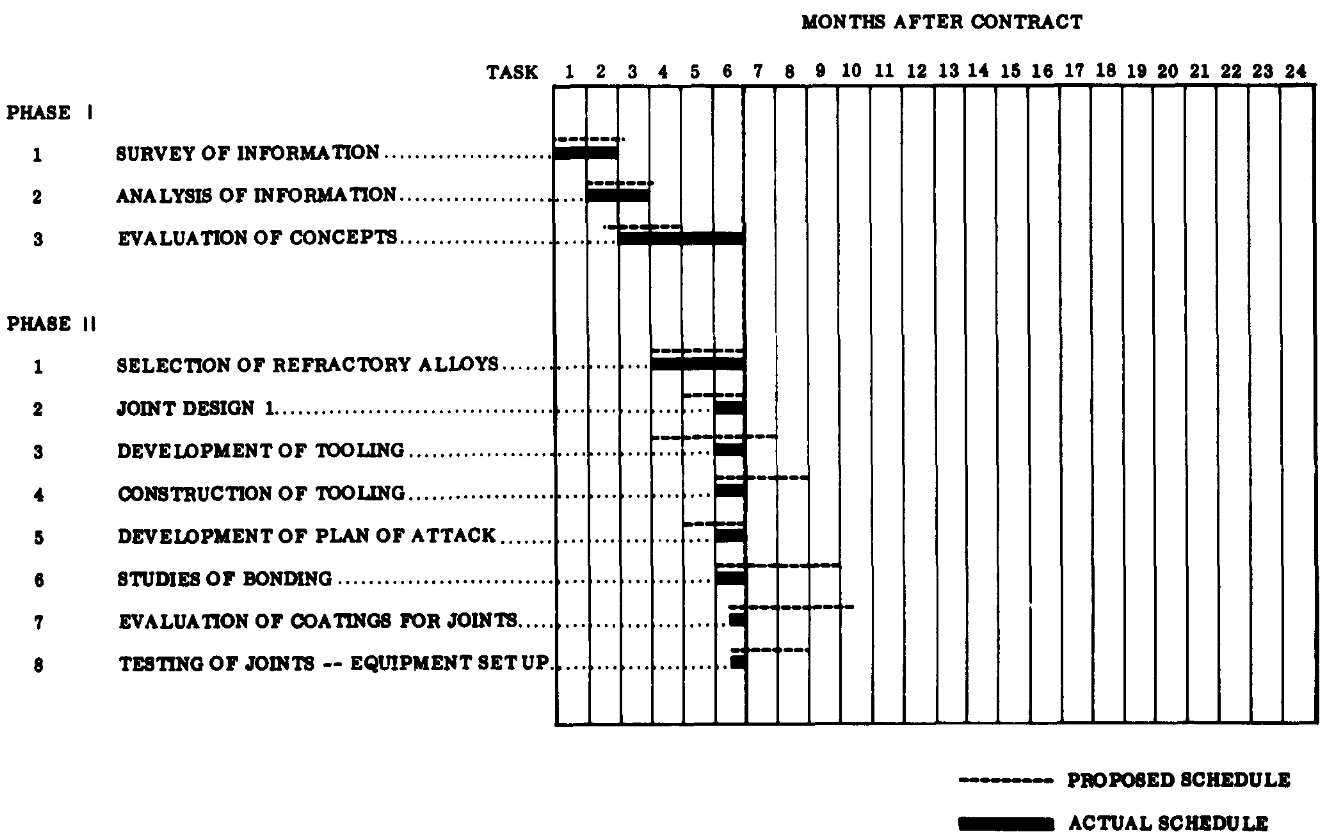


FIGURE 39. SCHEDULE FOR DIFFUSION BONDING PROGRAM

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